

Extraction and Purification of Dimeric Fullerene Oxides from Fullerene Soot

H. Takahashi, K. Tohji,* and I. Matsuoka

Department of Geoscience and Technology, Tohoku University, Sendai, 980-8579, Japan

B. Jeyadevan

Department of Geoscience, Mining Engineering and Materials Processing, Akita University, Akita, 010-0852, Japan

A. Kasuya, S. Ito, and Y. Nishina

Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan

T. Nirasawa

Bruker Japan Co. LTD, 3-21-5 Ninomiya Tsukuba, 305-0051, Japan

Received: December 19, 1997; In Final Form: May 4, 1998

In this paper, a novel method called hydrothermally initiated dynamic extraction (HIDE) is proposed for the extraction of dimeric fullerene oxides such as $C_{120}O$ and $C_{130}O$ in the fullerene soot. In this method, the soot is hydrothermally treated prior to the extraction by organic solvent. As a result, a few types of dimeric fullerene oxides were efficiently extracted from the soot for the first time. The extraction efficiency was 40 times more than that of the Soxhlet extraction with organic solvents, and several dimeric fullerene oxides were obtained in milligram quantities. Furthermore, the analyses strongly indicated that the extract contains not only dimeric fullerene oxides but also higher fullerene oxides. The detailed purification procedures for each dimeric fullerene oxide are also presented in this report.

Introduction

The synthesis of the dimeric fullerene oxides such as $C_{120}O$ was stimulated by the discovery of the odd-numbered clusters^{1–3} and Taylor's proposed mechanism for the generation of C_{119} via thermal decarbonylation of $C_{60}O$ and addition of the resultant C_{59} to C_{60} .⁴ This hypothesis suggested that the dimeric fullerene oxides could serve as an important precursor for the synthesis of odd-numbered fullerenes such as C_{119} and C_{129} . Recently, a new C_{60} derivative with the elemental composition $C_{120}O$ has been synthesized with a mixture of $C_{60}/C_{60}O$,^{5–7} and Gromov et al. also reported the production and characterization of C_{119} from $C_{120}O$ in large quantities.⁸ It is believed that this work will generate interest in the study of new fullerene derivatives, the odd-numbered fullerenes and dimeric fullerenes.^{9,10}

Lebedkin et al. have reported a simple and easy preparation method for $C_{120}O$ and oligomeric C_{60} oxide derivatives. In this method, the above derivatives are produced by heating the $C_{60}/C_{60}O$ mixture in an argon atmosphere at 473 K.⁵ Likewise, the dimeric fullerene oxides have been synthesized at temperatures around 473 K. In fact, it is long known that $C_{60}O$ occurs as an impurity in fullerene production by the arc method and is believed that the reaction environment necessary for the synthesis of fullerene oxides and dimeric oxides exists in the arc discharge chamber. Therefore, many types of oxidic fullerenes such as $C_{120}O$ are, of course, produced along with $C_{60}O$ but hidden in the soot because of the strong interaction with the soot. As a result, the extractable fullerene oxides other than $C_{60}O$ and $C_{70}O$ are very little and there are no reports on the extraction of the dimeric fullerene oxides from the soot using Soxhlet.

It is also known that large amounts of unextractable fullerenes still exist in the residual soot even after the extraction with organic solvents.^{11–13} Thus, it is believed that these unextractable fullerenes include the dimeric fullerene oxides that are deeply trapped in and/or strongly adsorbed to the amorphous-like carbon in the soot and do not come into contact with the organic solvent. To extract these fullerenes, it is rather important to break the soot into nanosize particles and to increase the surface area exposed to the solvent.

In the previous brief report, a novel and simple extraction method called hydrothermally initiated dynamic extraction (HIDE)^{14,15} was presented for the extraction of higher fullerenes over C_{90} .^{16,17} In this method, prior to the extraction by organic solvent, the soot is treated in boiling water that does not dissolve fullerenes and produces minimal byproducts. It is believed that the hydrothermal treatment brings about a dramatic change in the morphology of the soot, perhaps opening up the soot particles and thereby exposing these trapped species to the organic solvents in the next processing step.

In this report, we show that the extraction of considerable amounts of oxides and dimeric oxides is possible through the application of the HIDE method. Furthermore, we confirm that the various oxides are not produced in the HIDE process by (a) controlled leaking of oxygen into the generator, which changes the fullerene oxide concentration in the soot, and (b) the unsuccessful extraction of apparently rather pure fullerene soot.

Experimental Section

The fullerene soot was prepared through a dc arc discharge of graphite rod in a He atmosphere.¹⁸ The graphite rod of 99.997% purity (6 mm diameter and 150 mm long) was used as a positive electrode, and a graphite plate (3 cm × 3 cm square,

* To whom correspondence should be addressed. E-mail: tohji@ni4.earth.tohoku.ac.jp.

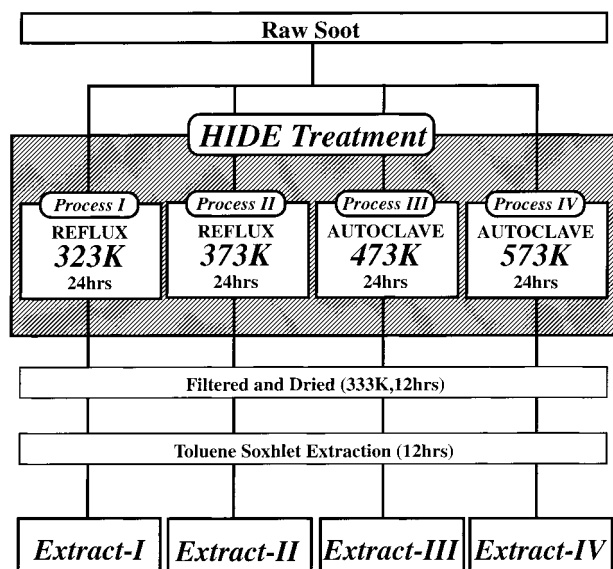


Figure 1. Flow chart for the preparation of the extracts using HIDE treatment.

2 cm thick) of 99.99% purity was used as a negative electrode. The arc discharge was carried out under a He pressure of 100 Torr and a discharge current of 100 A. The electrode gap was maintained less than 0.1 mm. The soot produced was collected from all parts of the chamber and homogenized thoroughly and used for all the experiments shown in Figure 1. The ratio of amorphous carbon to fullerene can be different among soots collected from different parts of the chamber. Therefore, homogenization was carried out to level out this difference. First, for processes I–IV in Figure 1, 50 mg of soot was taken for each process and sonicated in 100 cm³ (processes I and II) and 15 cm³ (process III and IV) of water for 10 min. In processes I and II, the samples were introduced into flasks with reflux attachments and heated at 323 and 373 K for 24 h, respectively. In processes III and IV, the samples were introduced into an autoclave and treated at 473 and 543 K for 24 h, respectively. The processed soot was withdrawn, filtered with a membrane filter of 0.1 mm pore size, dried at 333 K for 12 h, and Soxhlet extracted with 100 mL of organic solvents such as toluene, 1,2,4-trichlorobenzene (TCB), and carbon disulfide (CS₂). Quantitative analyses of the extracts were done with a high-performance liquid chromatograph (HPLC) using a Wakosil II 5C18 monomeric octadecylsilica column (ODS) of Wako Chemical Co. LTD, Japan, with a diameter of 4.6 mm and a length of 150 mm. A solution of toluene and methanol mixed in a ratio of 1:1 was used as the mobile phase at a rate of 1.0 mL/min. The measurements were carried out at an absorption wavelength of 330 nm. Mass analyses of fullerenes by matrix-assisted laser desorption ionization mass spectrometry (MALDI-TOF MS) have been done on samples fractionated by a Buckyclutcher column of Regis Technologies with a diameter of 20 mm and a length of 500 mm. Mass spectra were measured with a REFLEX III model of Bruker Co. LTD, Germany, with an N₂ laser using 9-nitroanthracene as a matrix. The UV–vis and the FT-IR absorption spectra of the isolated fullerenes were carried out using model U-2000 of Hitachi Co. LTD, Japan, and model FT-200 of Horiba Co. LTD, Japan, respectively.

Results and Discussion

Extraction of the Dimeric Fullerene Oxides from Soot.

Figure 2 shows the HPLC profiles of toluene extracts with and without HIDE treatment for fullerene soot prepared under the

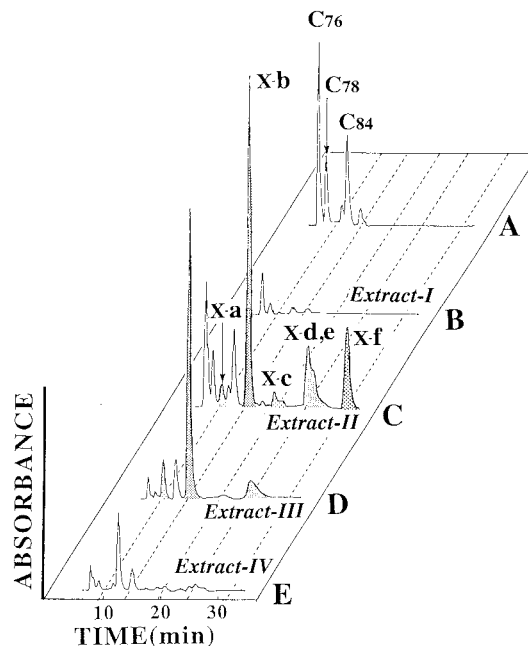


Figure 2. HPLC profiles of the extracts. Spectrum A corresponds to the toluene extract without HIDE treatment. Spectra B–E correspond to the extracts I–IV. Peaks Xa–Xf show the newly extracted fullerenes by HIDE treatment.

conditions stipulated in the Experimental Section. It can be seen that the HPLC profile of toluene extract without HIDE treatment shown in Figure 2A agree well with an earlier report.¹⁹ In the case of extract I shown in Figure 2B, the new species and higher fullerenes such as C₇₆ and C₈₄ do not appear because at 323 K the soot remain coagulated because of hydrophobicity and because the energy of water molecules was not sufficient to disintegrate the soot particles. In contrast, the HPLC profile seen in Figure 2C shows the presence of several new species compared with those of spectra A and B of Figure 2. Therefore, it is clear that the new species from Xa to Xf were extracted as a result of HIDE treatment at 373 K (extract II). Further, to determine the optimum temperature and pressure conditions for the extraction of any fullerene species through HIDE treatment, experiments were carried out at different temperature and pressure conditions. Spectra D and E of Figure 2 show the HPLC profiles of the toluene extracts III and IV, which were obtained from HIDE-treated soots at 473 and 543 K, respectively. The horizontal scale in Figure 2 is the same for all the spectra, and the efficiency of fullerene extraction under different conditions can be compared. Since the absorption peaks of C₆₀ and C₇₀ are very strong at a wavelength of 330 nm, these two peaks are not shown in Figure 2. Further, since the monomeric ODS stationary phase elutes fullerenes by molecular weight, peaks other than Xa are believed to represent fullerenes higher than C₈₄.²⁰

As seen in the HPLC profiles of extracts III and IV shown in spectra D and E of Figure 2, the intensities of the peaks of the new species assigned from Xa to Xf decreased as the processing temperature was increased. Furthermore, the intensities of the higher fullerenes peaks such as C₇₆, C₇₈, and C₈₂ were also decreased. Therefore, it is believed that the pressure and temperature conditions used for the hydrothermal treatment in extracts III and IV are not appropriate for the extraction of C₇₆, C₇₈, C₈₂, or the new species shown in extract II. However, the hydrothermal treatment at 543 K is effective for the extraction of C₈₄ and the amount of extractable C₈₄ increased

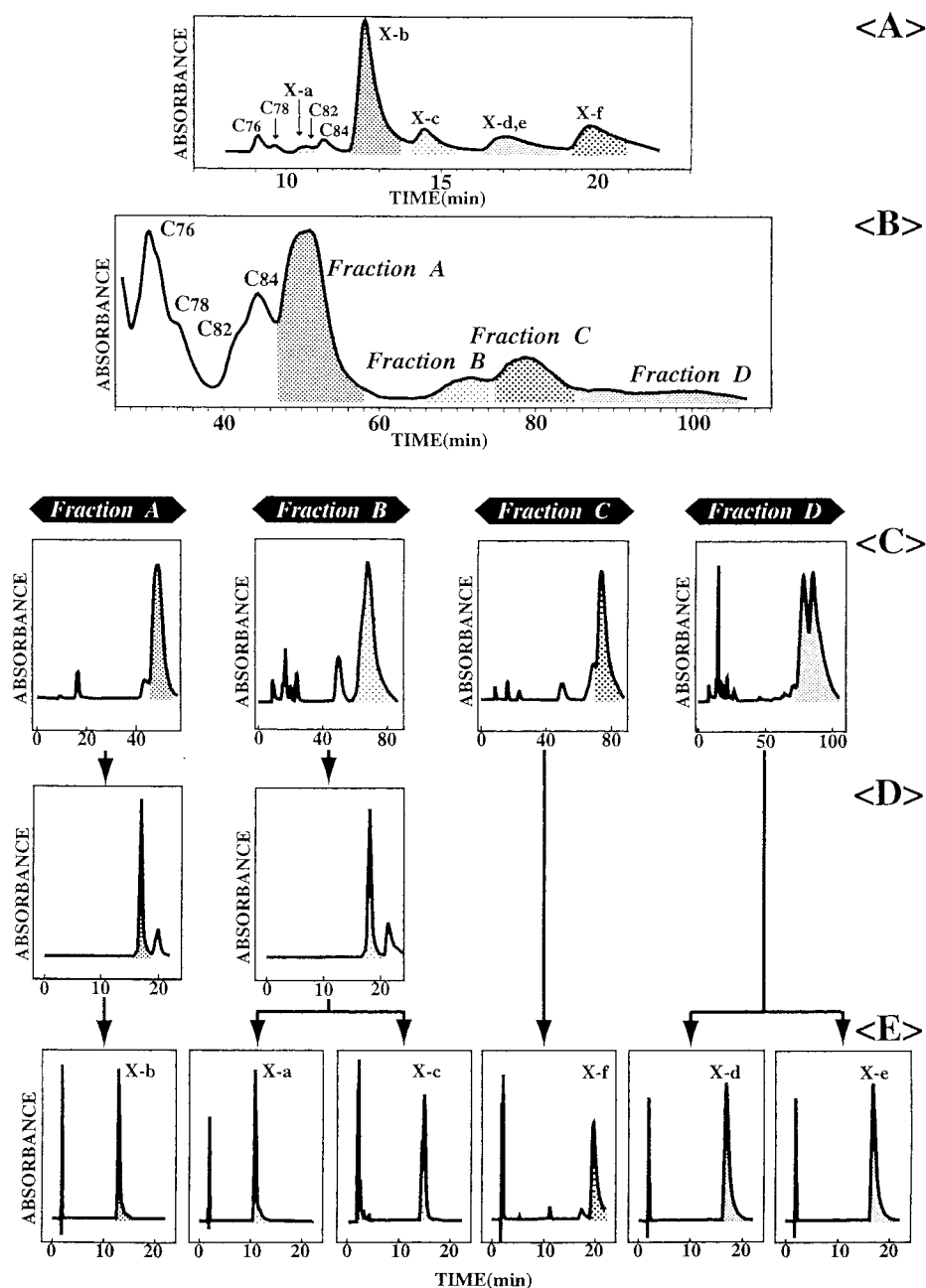


Figure 3. HPLC profiles of the samples in the purification and isolation processes. Part A is the HPLC profile of the toluene extract obtained using an analytical Wakosil II 5C18 ODS column and a 1:1 toluene/methanol mixture as eluent. Part B is the HPLC profile of the toluene extract measured by the Buckyclutcher column and a 1:1 toluene/*n*-hexane mixture as eluent. The fractions A–D were collected in the first purification step. Part C shows the HPLC profiles of fractions A–D obtained using the Buckyclutcher column and a 1:1 toluene/*n*-hexane mixture as eluent. Part D shows the HPLC profiles of fractions A and B obtained using the Buckyclutcher column and 100% toluene as eluent. Part E shows the HPLC profiles of the final products obtained using an analytical Wakosil II 5C18 ODS column and a 1:1 toluene/methanol mixture as eluent.

by about 2.5 times compared with that of the sample treated at 373 K and ambient pressure.

Considering the characteristics of the monomeric ODS column used, the retention time of the peak Xa corresponds to the C₇₈ isomer, C₈₀, and C₈₂O. By comparison of the HPLC profile of the pure C₉₀ measured under the same conditions, peaks Xb and Xc were estimated to represent higher fullerenes around C₉₀ and/or their oxides. Furthermore, the peaks Xd, Xe, and Xf are assumed to represent fullerenes higher than C₉₀. Therefore, the HIDE treatment has made the extraction of the fullerenes specified by peaks Xa–Xf from the soot for the first time. And also, if we compare the peak intensity of Xb between toluene extracts with and without HIDE treatment, almost 40 times the increase can be observed.

The extraction efficiencies of giant fullerenes are reported to be a function of the solvents. They are more extractable in solvents such as 1,2,4-TCB, pyridine, and CS₂ than in toluene.^{11–13,21–30} However, there is no considerable difference among the HPLC profiles of the extracts in toluene, CS₂, or 1,2,4-TCB obtained from the HIDE-treated soot. Therefore, it is believed that all the above solvents are capable of dissolving the new fullerene species.

Purification Procedure for the New Species. As seen in Figure 3A, many kinds of fullerene species are contained in toluene extracts. Therefore, to select an effective separation and isolation scheme, a few HPLC columns widely used for the separation of fullerenes have been examined. The experiments led to the following separation and isolation scheme for

the newly extracted fullerenes. In the first stage, the toluene extract was separated in an HPLC system (Waters 600E) with the Buckyclutcher column and 1:1 toluene/*n*-hexane mixture as eluent. Owing to the characteristic of the Buckyclutcher column, the retention time of the newly extracted species became longer in comparison with that of ODS column using 1:1 toluene/methanol mixture as eluent. In this stage, four fractions shown in Figure 3B were collected and the HPLC profiles of the fractionated samples are shown in Figure 3C. In the next stage, for further separation and purification of the fractions shown in Figure 3C, an HPLC system with a Buckyclutcher column using a 1:1 toluene/*n*-hexane mixture as eluent was used again. In the final stage, the purification of fractions A and B was performed with the Buckyclutcher column using 100% toluene as eluent and shown in Figure 3D. The main peak in the fraction A was completely separated from C₈₄, and, on the other hand, the main peak in the fraction B consisted of two species. In total, six fractions as shown in Figure 3E were obtained, where the analyses have been done using an analytical column using 1:1 toluene/methanol mixture as eluent. As a result, hitherto unreported HPLC peaks from Xa to Xf were completely isolated and the sequence of the extracted species was found to be Xb, Xa, Xc, Xf, Xd, and Xe in the Buckyclutcher column.

Identification of the New Species Extracted Using the HIDE Method. The mass spectra of the isolated species Xb, Xd, and Xf are shown in Figure 4. The mass spectrum of Xa consists of a strong peak of C₈₂ and a weak peak of C₈₂O. The retention time of Xa was shorter than that of C₈₂, and the fragmentation pattern of Xa looked similar to that of the fullerene oxides. The mass spectrum of Xb shown in Figure 4A, however, consists of three main peaks, namely, C₆₀, C₆₀O (720 and 736 amu), and C₁₂₀O (1456 amu). Considering the retention time of Xb in the HPLC, there is no possibility for the presence of either C₆₀ or C₆₀O. Therefore, it is believed that the two peaks corresponding to C₆₀ and C₆₀O are due to the fragmentation of C₁₂₀O.

The HPLC and mass analyses results of Xc are consistent with each other. The main species is C₉₀, and the weak peaks due to C₈₈, C₉₂, C₉₄, and C₉₆ are observed.

The mass spectrum of Xd shown in Figure 4B consists of the peaks C₆₀, C₆₀O, C₇₀, C₇₀O, and C₁₃₀O. The fragmentation pattern looks similar to the case of C₁₂₀O. Therefore, we believe that the peak Xd corresponds to C₁₃₀O that has a mass number of 1576 amu. The mass spectrum of Xe was quite similar to that of Xd.

As seen in Figure 4C, the mass number of Xf is the same as that of Xd and Xe. However, the intensities of C₆₀O and C₇₀O peaks are weaker than those of Xd and Xe. Therefore, it seems that the Xf is also an isomer of C₁₃₀O.

The UV-vis spectra of fractions corresponding to Xb, Xd, Xe, and Xf resemble that of C₆₀, although they show much broader features. The 435 nm band usually observed for C₆₀ monoadducts is absent except in the cases of Xa and Xc. As seen in Figure 5, the FT-IR spectra of Xb, Xd, and Xf show a splitting of the original C₆₀ vibrations into subfeatures, indicating a decrease of symmetry.³¹ In particular, the bands between 1000 and 1100 cm⁻¹ are near the characteristic region of the C—O—C stretching vibration of cyclic ethers. The FT-IR spectrum of Xf is, however, much broader than that of Xd. As stated in ref 5, the existence of this vibrational band is indicative of a dimeric fullerenes structure.

The spectroscopic data of Xb such as the UV-vis, the FT-IR spectra and the retention time in the HPLC agreed with those

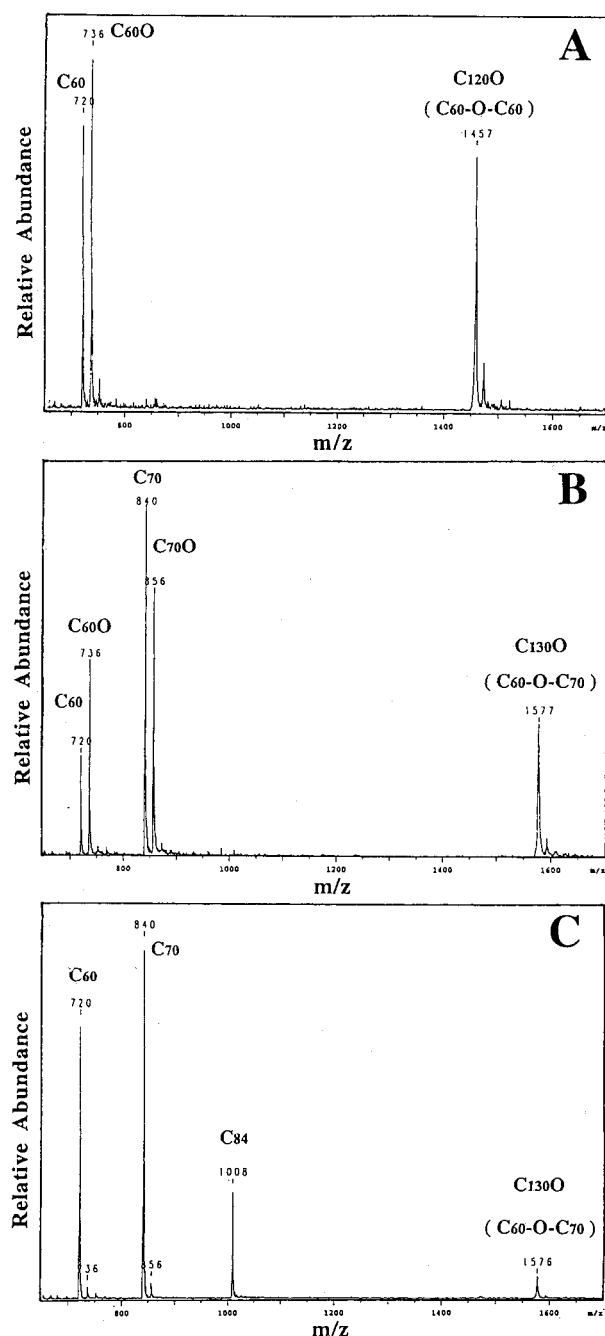


Figure 4. Parts A, B, and C are MALDI-TOF mass spectra of the isolated species Xb, Xd, and Xf, respectively.

of the synthesized dimeric C₆₀ fullerene oxide.⁵ Taking into account the experimental data, it is believed that the newly extracted species, C₁₂₀O, from the soot has the same structure as that of C₁₂₀O synthesized from the mixture of C₆₀ and C₆₀O. Furthermore, it seems that the structure of C₁₃₀O³² is similar to that of C₁₂₀O. As discussed in the previous section, it has been found that there are at least three C₁₃₀O isomers, namely, peaks Xd, Xe, and Xf in Figure 2. Unfortunately, we have not yet been able to determine the structures of these isomers by NMR using samples having C₁₃ in natural abundance.

Are the New Species Synthesized during HIDE Treatment? The dimeric fullerene oxide, C₁₂₀O, has been produced at a temperature around 473 K.⁵ This environment, of course, exists in the arc discharge chamber. Therefore, we believe that the dimeric fullerenes oxides have been synthesized in the arc chamber because of the reaction with the arc products such as

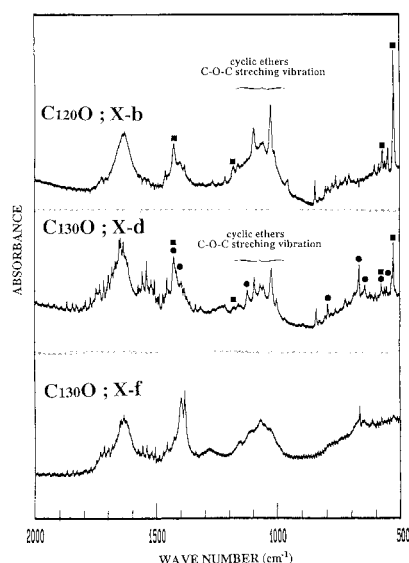


Figure 5. FT-IR spectra of the isolated species Xb, Xd, and Xf, where black squares and circles show the original C_{60} and C_{70} vibrations, respectively.

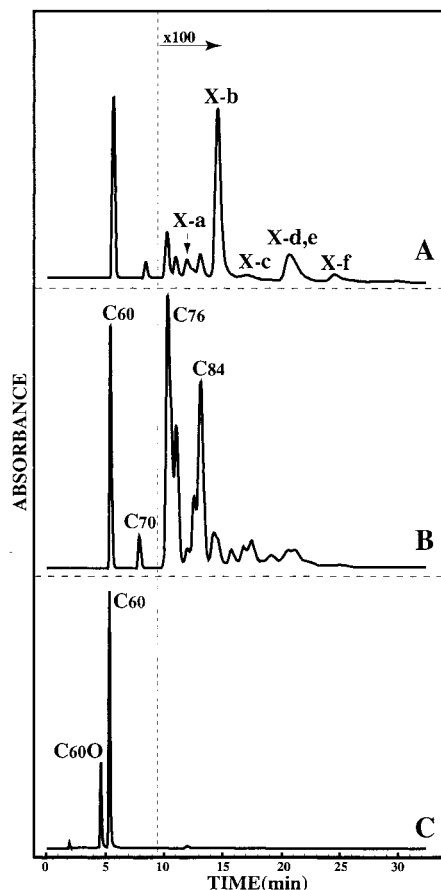


Figure 6. Parts A and B are HPLC profiles of the toluene extracts from soots A and B, respectively. Part C is HPLC profile of the soluble species in the products made by reacting with C_{60} and $C_{60}O$ in water.

C_{60} and $C_{60}O$. However, it may also be argued that the new species are formed during HIDE treatment. Parts A and B of Figure 6 show the HPLC profiles of the extracts for two different samples treated using the HIDE method. The soots of parts A and B are the soots prepared under optimized conditions for the formation of fullerene oxides and under conditions that are as clean as possible, respectively. If the new species are assumed to have formed during the treatment, we could expect

both of these extracts to be rich in new fullerenes and fullerene oxide species. However, the presence of the new fullerene species is confirmed only in the extract of soot A and not in the extract of soot B. The amount of $C_{60}O$ before and after HIDE treatment was the same in soots A and B. Furthermore, as shown in Figure 6C, these new fullerenes have been hardly synthesized with a mixture of $C_{60}/C_{60}O$ in boiling water of neutral pH.

Transmission electron microscopy (TEM) observations of the soot samples prior to and after hydrothermal treatment do not show any visible changes. Though the exact mechanism behind the success of HIDE treatment is not clear, the experimental results confirm that the extraction of the new fullerene species depends only on the type of soot; it is not generated during the hydrothermal treatment. However, further work is necessary to determine the exact mechanism responsible for the successful extraction of the new species reported in this paper.

From the above set of experiments, it could be said that (a) within the experimented temperature and pressure conditions, the hydrothermal treatment at 373 K and ambient pressure is ideal for the extraction of the dimeric fullerene oxides, (b) several dimeric fullerene oxides ($C_{120}O$ and $C_{130}O$) were extracted in milligram quantities for the first time, and (c) all dimeric fullerene oxides are unstable at temperatures higher than 573 K.

It could be concluded that the HIDE treatment used here brings forth a dramatic change in the fullerene-soot environment. For example, owing to the change in the morphology of the soot and/or when the soot particles are opened up (not to an extent where observation is possible with TEM), the trapped species are exposed to the organic solvents or it may be that the water molecules modify the adsorption mechanism between dimeric fullerene oxide and soot and make easy the removal of the novel fullerene species using organic solvents.

Acknowledgment. We would like to thank Professor Wolfgang Krätschmer of the Max-Planck Institute for valuable discussions. We greatly thank Professor Hisanori Shinohara of Nagoya University for providing us with a pure C_{90} sample and for valuable discussions. We thank Mr. Katsushi Obata of Tohoku Science Co. Ltd. for advice on the separation of the dimeric fullerene oxides. This work is supported in part by CREST of Japan Science and Technology Institute, by a Grant-in-Aid for Priority Research in 1997 from the Ministry of Education, Science, Culture and Sports of Japan and by Izumi Science and Technology Foundation.

References and Notes

- (1) McElvany, S. W.; Callahan, J. H.; Ross, M. M.; Lamb, L. D.; Huffman, D. R. *Science* **1993**, *260*, 1632.
- (2) Dang, J. P.; Ju, D. D.; Her, G. R.; Mou, C. Y.; Chen, C. J.; Lin, Y. Y.; Han, C. C. *J. Phys. Chem.* **1993**, *97*, 11575.
- (3) Beck, R. D.; Brauchel, G.; Stoermer, C.; Kappes, M. M. *J. Chem. Phys.* **1995**, *102*, 540.
- (4) Taylor, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1629.
- (5) Lebedkin, S.; Ballenweg, S.; Gross, J.; Taylor, R.; Krätschmer, W. *Tetrahedron Lett.* **1995**, *36*, 4971.
- (6) Gromov, A.; Lebedkin, S.; Ballenweg, S.; Krätschmer, W. *Fullerenes and Fullerene Nanostructure, Proceedings of the International Winterschool on Electronic Properties of Novel Materials*; Kuzmany, H., Fink, J., Mehring, M., Roth, S., Eds.; World Scientific: Singapore, 1996; p 460.
- (7) Smith, A. B.; Tokuyama, H.; Strongin, R. M.; Furst, G. T.; Romanow, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 9359.
- (8) Gromov, A.; Ballenweg, S.; Giesa, S.; Lebedkin, S.; Hull, W. E.; Krätschmer, W. *Chem. Phys. Lett.* **1997**, *267*, 460.
- (9) Strout, D. L.; Murry, R. L.; Xu, R. L.; Eckhoff, W. C.; Odom, G. K.; Scuseria, G. E. *Chem. Phys. Lett.* **1993**, *214*, 576.
- (10) Matsuzawa, N.; Ata, M.; Dixon, D. A.; Fitzgerald, G. *J. Phys. Chem.* **1994**, *98*, 2555.

- (11) Shinohara, H.; Sato, H.; Saito, Y.; Izuoka, A.; Sugawara, T.; Ito, H.; Sakurai, T.; Matsuo, T. *Mass Spectrom.* **1992**, 6, 413.
- (12) Smart, C.; Eldrige, B.; Reuter, W.; Zimmerman, J. A.; Creagy, W. R.; Rivera, N.; Ruoff, R. S. *Chem. Phys. Lett.* **1992**, 188, 171.
- (13) Lamb, L. D.; Huffman, D. R.; Workman, R. K.; Howells, S.; Chen, T.; Sarid, D.; Ziolo, R. F. *Science* **1992**, 255, 1413.
- (14) Tohji, K.; Goto, T.; Takahashi, H.; Shinoda, Y.; Shimizu, N.; Jeyadevan, B.; Matsuoka, I.; Saito, Y.; Kasuya, A.; Ohsuna, T.; Hiraga, K.; Nishina, Y. *Nature* **1996**, 383, 679.
- (15) Tohji, K.; Takahashi, H.; Shinoda, Y.; Shimizu, N.; Jeyadevan, B.; Matsuoka, I.; Saito, Y.; Kasuya, A.; Ito, S.; Nishina, Y. *J. Phys. Chem. B* **1997**, 101, 1974.
- (16) Takahashi, H.; Akiyama, Y.; Goto, T.; Jeyadevan, B.; Tohji, K.; Matsuoka, I. *J. Mater. Sci. Eng.* **1996**, A217/218, 42.
- (17) Takahashi, H.; Jeyadevan, B.; Tohji, K.; Matsuoka, I.; Kasuya, A.; Nishina, Y.; Nirasawa, T. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1996; Vol. 3, p 72.
- (18) See, for example, the following. (a) Tohji, K.; Paul, A.; Moro, L.; Malhotra, L.; Lorents, D. C.; Ruoff, R. S. *J. Phys. Chem.* **1995**, 99, 17785. (b) Haufler, R. E. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 1, pp 50–67. (c) Tohji, K.; Saito, K.; Matsuoka, I.; Sogabe, T.; Nagasawa, K.; *Fullerene Sci. Technol.* **1997**, 5, 33. (d) Tohji, K.; Saito, K.; Matsuoka, I.; Sogabe, T.; Nagasawa, K. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 1, pp 132–140.
- (19) Jinno, K.; Uemura, T.; Ohta, H.; Nagashima, H.; Ito, K. *Anal. Chem.* **1993**, 65, 2650.
- (20) Jinno, K.; Matsui, H.; Ohta, H.; Saito, Y.; Nakagawa, K.; Nagashima, H.; Ito, K. *Chromatographia* **1995**, 41, 353.
- (21) Parker, H. D.; Wurz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, 113, 7499.
- (22) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wand, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, 95, 7564.
- (23) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, 252, 548.
- (24) Diederich, F.; Whetten, R. L.; Thilgen, C.; Ettl, R.; Chao, I.; Alvarez, M. M. *Science* **1991**, 254, 1768.
- (25) Shinohara, H.; Sato, H.; Saito, Y.; Takayama, M.; Izuoka, A.; Sugawara, T. *J. Phys. Chem.* **1991**, 95, 8449.
- (26) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Suzuki, S.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, 357, 142.
- (27) Scrivens, W. A.; Tour, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1207.
- (28) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, 97, 3379.
- (29) Diederich, F.; Whetten, R. L. *Acc. Chem. Res.* **1992**, 25, 119.
- (30) Thilgen, C.; Diederich, F.; Whetten, R. L. *Buckminsterfullerenes*; Billups, W. E., Ciufolini, M. A., Eds.; VCH Publishers: New York, 1993; p 59.
- (31) Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, 126, 1061.
- (32) Fowler, P. W.; Mitchell, D.; Taylor, R.; Seifert, G. *J. Chem. Soc., Perkin Trans.* **1997**, 2, 1901.