Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2006, 16(2), 77–78

Mendeleev Communications

Non-chromatographic method for the large-scale isolation of C_{60} from a fullerene extract

Pavel A. Troshin,* Vyacheslav M. Martynenko and Rimma N. Lyubovskaya

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 515 5420; e-mail: troshin@cat.icp.ac.ru

DOI: 10.1070/MC2006v016n02ABEH002285

Differences in the properties of brominated C_{60} and C_{70} allowed us to develop an efficient and rapid procedure for the isolation of C_{60} from a fullerene extract.

Since fullerenes became available in bulk, a number of promising applications of parent C_{60} and its derivatives were discovered.[1] Particularly, [60]fullerene-conjugated polymer composites are used for the fabrication of flexible organic solar cells.[2] The use of novel materials based on [60]fullerene is limited by its relatively high cost that reflects a number of challenges in its production process. Destruction of graphite or amorphous carbon under various conditions, combustion of hydrocarbons and other routes afford fullerene soot that contains 10–30% fullerenes. The treatment of the fullerene soot with organic solvents followed by concentration of the resulting solution gives a fullerene extract as a mixture of C_{60} (usually 80–85%), C_{70} (15–17%) and higher fullerenes (C_{76}, C_{78}, *etc*., 1–5%). Time- and solvent-consuming column chromatography on special stationary phases (such as porous charcoal) was commonly used for the isolation of C_{60} and C_{70} from the fullerene extract.[3] The separation of fullerene extracts using differences in the chemical properties of C_{60} and C_{70} was also attempted. Particularly, the selective complexation of fullerenes with calixarenes[4] or aluminium chloride[5] was reported. However, these methods were never applied in fullerene production technology and even for custom isolation of small batches of C_{60} or C_{70}. The reasons are most likely in high costs of starting materials (calixarenes), moderate discrimination between C_{60} and C_{70} cages and difficulties with washing out organic and inorganic guests from their complexes with fullerenes.

The first efficient separation method based on differences in the reactivity of C_{60} and C_{70} has been reported recently.[6] It was observed that C_{70} and higher fullerenes react with the organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) faster than C_{60}. Thus, the titration of a fullerene extract with DBU in toluene affords predominant precipitation of C_{70}-DBU and similar complexes of higher fullerenes leaving C_{60} in solution. Unfortunately, it is impossible to recover C_{70} and higher fullerenes from their complexes with DBU.

Fullerene C_{60} isolated by column chromatography or using a DBU-based method contains 4–5% solvent trapped in the crystal packing and an amount of absorbed water.[7] The vacuum sublimation of fullerene is required to get rid of the solvent impurities. Here, we report a facile non-chromatographic method for the rapid isolation of pure C_{60} from the fullerene extract that gives solvent-free C_{60} in 85–90% yield.

Previously, we studied the bromination of fullerenes under various conditions, particularly, in neat bromine.[8] The bromination of both C_{60} and C_{70} proceeds as a step-by-step process (Scheme 1). The careful control of the duration of bromination allows for isolation of individual products with specific compositions and structures as was determined previously using X-ray single crystal diffraction.[8] The first product of C_{60} bromination ($C_{60}Br_8$) possesses low solubility in bromine; in contrast, $C_{70}Br_8$ formed under the same conditions exhibited outstanding solubility in liquid bromine (150–200 mg ml^{-1}).

$$C_{60} \xrightarrow{\text{5–15 min}} \underset{\substack{\text{insoluble}\\ \text{in bromine}}}{C_{60}Br_8{\cdot}nBr_2} \xrightarrow{\text{20–80 min}} C_{60}Br_{14} \xrightarrow{\text{6–8 h}} C_{60}Br_{24}$$

$$C_{70} \xrightarrow{\text{5–15 min}} \underset{\substack{\text{insoluble}\\ \text{in bromine}}}{C_{70}Br_8} \xrightarrow{\text{6–12 h}} C_{70}Br_{10}$$

Scheme 1

Such a remarkable difference in the solubility of $C_{60}Br_8$ and $C_{70}Br_8$ in liquid bromine permits facile separation of these bromofullerenes. For this purpose, 30 g of the fullerene extract were introduced in small portions into a flask with 100–130 ml of bromine for 3–4 min. The reaction is exothermic; therefore, bromine should be previously cooled in an ice bath to –5–0 °C. Immediately after addition of the fullerene extract, the reagent mixture was stirred for 5 min and then kept without stirring for 10 min at room temperature to precipitate $C_{60}Br_8{\cdot}nBr_2$ (n = 1, 2[8(b)]). The precipitate was filtered off under reduced pressure through a glass filter and dried in a stream of nitrogen to avoid contact with air moisture.

Thermal gravimetry (TG) and differential scanning calorimetry (DSC) measurements showed that $C_{60}Br_8{\cdot}nBr_2$ undergoes one-step decomposition at 100–120 °C to parent C_{60} and bromine; $C_{60}Br_{14}$ and $C_{60}Br_{24}$ also decompose below 200 °C. Low thermal stability of bromofullerenes is most likely a result of a sterical hindrance of eclipsed bromine atoms attached to the carbon cage. Therefore, the debromination of $C_{60}Br_8{\cdot}nBr_2$ was easily performed by heating the material in a high vacuum (10^{-3} Torr) at 200 °C for 20 min. The weight of isolated C_{60} (23 g) corresponded to nearly 90% performance of the separation procedure. The concentration of $C_{70}Br_8$ solution in bromine and following debromination of the residue (10^{-3} Torr, 200 °C, 40 min) afforded 6.5 g of C_{70}-enriched material that can be further purified by chromatography. Bromine that is formed during the decomposition of brominated fullerenes should be collected in the catcher cooled with liquid nitrogen; it can be then recycled by distillation with phosphorous anhydride.

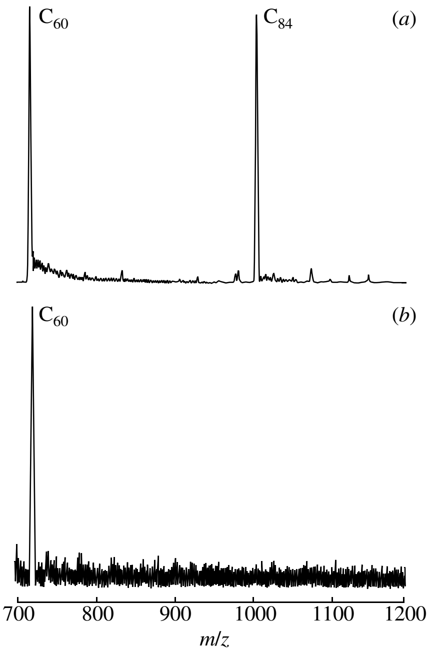

Figure 1 LDI mass spectra of (*a*) C_{84} enriched and (*b*) isolated C_{60} samples.

The purity of the prepared sample of [60]fullerene was checked initially by LDI mass spectrometry. A very intense signal of the C_{60}^+ ion at m/z 720, low intensity peaks at m/z 840 (C_{70}^+) and 1008 (C_{84}^+) were also observed in the mass spectrum. The HPLC profile also proved a relatively high purity of C_{60} (94–97%). Mass-spectrometric analysis (EI) of gases evolved by C_{60} powder under gradual heating in the range 20–350 °C (10^{-1} Torr) evidenced the presence of absorbed molecular nitrogen, oxygen and water, while no traces of brominated hydrocarbons (the starting fullerene extract contained 4–5% of solvents) were observed. Very low-intensity peaks of Br_2 also appeared at 110–350 °C; most likely, bromine was absorbed by fullerene like nitrogen and water.

Repeated bromination–debromination procedures did not result in further purification of C_{60} from C_{70} and C_{84} impurities. The presence of C_{70} can be explained by co-crystallization of $C_{60}Br_8$ with a small amount of $C_{70}Br_8$ during the precipitation of the material from bromine. The selective extraction of C_{84} from other higher fullerenes was surprising. To rationalise this result, a C_{84}-containing sample of $C_{60}Br_8$ (5 g) was dissolved in liquid bromine (150 ml) with stirring at room temperature for 1 h. The filtration of the resulting solution afforded a small amount of a precipitate (~8 mg); this material was heated in a vacuum at 200 °C and then analysed by LDI mass spectrometry. The mass spectrum exhibited equal-intensity signals of C_{60} and C_{84} (Figure 1) thus indicating a high C_{84} content of this sample. The solution of $C_{60}Br_{14}$ was concentrated, and the residue was debrominated in a vacuum at 200 °C to give [60]fullerene powder. The LDI mass spectrum of this C_{60} sample did not show a signal of C_{84}; therefore, the described method can be applied to the purification of C_{60} and the isolation of small amounts of a C_{84}-enriched material.

Although the purity of C_{60} isolated by bromination–debromination procedure (94–97%) was lower than the purity of chromatographically isolated samples (99%), it seems acceptable for chemical purposes. We used home-isolated [60]fullerene as a precursor to various organic and inorganic derivatives of C_{60}; the NMR characterization of synthesised C_{60} derivatives and X-ray single-crystal diffraction did not reveal impurities of C_{70}-based compounds.

This work was supported by the Russian Foundation for Basic Research (grant no. 04-03-32870a), INTAS (grant no. 04-83-3733) and Russian Science Support Foundation.

References

1 *Perspectives of Fullerene Nanotechnology*, ed. E. Osawa, Kluwer Academic Publishers, Dordrecht, Boston, London, 2001.
2 H. Hoppe and N. S. Sariciftci, *J. Mater. Res.*, 2004, **19**, 1924.
3 A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, 1994.
4 J. L. Atwood, G. A. Koutsantonis and C. L. Raston, *Nature*, 1994, **368**, 229.
5 K. Kimata, H. Hosoya, T. Araki and N. Tanaka, *J. Org. Chem.*, 1993, **58**, 282.
6 K. Nagata, E. Dejima, Y. Kikuchi and M. Hashiguchi, *Chem. Lett.*, 2005, **34**, 178.
7 Yu. M. Shulga, V. M. Martynenko, S. A. Baskakov, Yu. V. Baskakova, G. A. Volkov, N. V. Chapysheva, V. F. Razumov and V. G. Sursaeva, *Mass-spektrometriya*, 2005, **2**, 223 (in Russian).
8 (*a*) P. A. Troshin, D. Kolesnikov, A. V. Burtsev, R. N. Lyubovskaya, N. I. Denisenko, A. A. Popov, S. I. Troyanov and O. V. Boltalina, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2003, **11**, 47; (*b*) S. I. Troyanov, P. A. Troshin, O. V. Boltalina and E. Kemnitz, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2003, **11**, 61; (*c*) P. A. Troshin, A. S. Astakhova and R. N. Lyubovskaya, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2005, **13**, 331; (*d*) S. I. Troyanov, A. A. Popov, N. I. Denisenko, O. V. Boltalina, L. N. Sidorov and E. Kemnitz, *Angew. Chem., Int. Ed. Engl.*, 2003, **115**, 2497.

Received: 1st December 2005; Com. 05/2627