

Convenient separation of high-purity C₆₀ from crude fullerene extract by selective complexation with AlCl₃

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ABSTRACT A purification procedure for C₆₀ from the fullerene extract has been developed using the differential complexation of C₆₀ and C₇₀ with AlCl₃ (or its conjugate acid) in CS₂ solution. In addition to pure C₆₀ (>99.8%), the procedure also provides C₇₀-enriched fullerene mixture.

Fullerenes have attracted considerable attention of chemists since their first practical preparation by Kratschmer *et al.* (1, 2). The separation/purification of C₆₀ from the fullerene extract, however, till now generally involved a chromatographic separation procedure with the use of large amounts of solvents (3–9), which is rather tedious and applicable only for smaller-scale operations. More recently, flash chromatographic procedures (10–12) have been developed using a slurry of alkaline decolorizing Norit A and silica gel as supports and toluene as eluent; these methods are useful for gram-scale purification of C₆₀. A differential complexation method based on calixarenes (host–guest interaction) has also been developed (13). We report here a convenient chemical separation of C₆₀ from the fullerene extract. The method is based on differential complexation of C₆₀, C₇₀, and higher fullerenes with various Lewis acids, of which we found AlCl₃ to be the best.

RESULTS AND DISCUSSION

The fullerene-containing soot was prepared in an in-house built “multibarrel” gravity-fed reactor (Fig. 1) that was designed to allow for consecutive resistive evaporation of nine graphite rods. This design simplifies the procedure and greatly reduces the effort required in the preparation of fullerenes compared with other published laboratory methods (ref. 14 and references cited therein). The reactor is constructed from a type 316 stainless steel base; a glass bell jar; oxygen-free hardened copper electrodes, contacts, and guides; high-purity graphite electrodes; Macor insulators, Varian copper high-current feedthroughs; and high-vacuum valves and fittings. In the process of resistive heating of graphite, substantial heat is generated. The size of the reactor is commensurate for the efficient dissipation of heat. Operation starts with evacuation and purging of the reactor with helium. After three evacuation/purge cycles the helium pressure is set to 100 mmHg (13.3 kPa). Next, the reactor’s stainless steel base is cooled by using a Neslab ULT-80DD low-temperature circulator to circulate methanol at –40°C in silicone rubber tubing wrapped around the base. By monitoring pressure changes, the reactor is safeguarded against excessive temperature surges. In the reactor we could fit nine 12-inch-long 1/8-inch-diameter high-purity graphite rods. By consecutively switching from one electrode to the next without breaking vacuum we were able to produce 23–27 g of fullerene-containing soot in 7–9 hr. Optimum yield of C₆₀ was achieved when 70–75 A of current at ≈50 V was used to

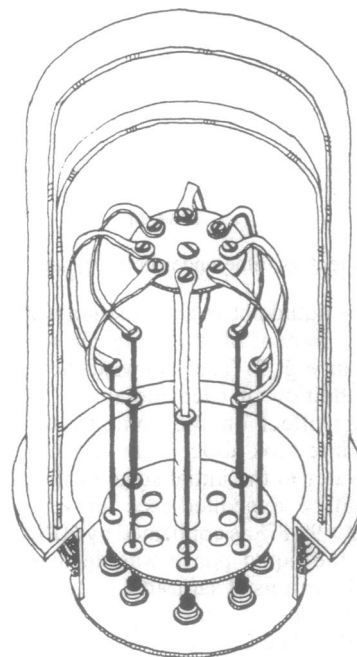


FIG. 1. “Multibarrel” fullerene generator.

resistively heat high-purity graphite. Under these conditions each rod is consumed in about 9 min. The produced soot was collected by a commercial vacuum cleaner with a paper dust-bag. The bags were then handled in an Aldrich Atmos-Bag, which made this otherwise messy operation manageable. Extraction of the soot with toluene and subsequent drying at 350°C in a tube furnace under argon purge afforded 9–11% yield of fullerene extract which contained 82% C₆₀ and 17% C₇₀ as determined by HPLC. The HPLC analysis was performed with photodiode array detector 168 using a Pirlce type 1A ionically bound phenylglycine column, 25 cm long with 10-mm inner diameter (purchased from Regis, Morton Grove, IL). Detection was carried out at 316 nm and 353 nm (dual channel detector) with hexane/toluene, 4:1 (vol/vol), as eluent at a flow rate of 2.0 ml/min.

In a typical separation 2.0 g of the fullerene extract was dissolved in 500 ml of CS₂ (commercial grade containing 0.05% water was used; Fisher) to which 80 g of AlCl₃ (anhydrous GR powder purchased from EM Science) was added and stirred at room temperature for 2–6 days. The procedure was carried out under both relatively dry conditions and with consecutive addition of 0.25-ml portions of water to a total of 1.25 ml of water. It was found that C₇₀ complexed much stronger and that the resulting complexes precipitated out of the CS₂ solution. As the complex formation progressed, the color of the liquid phase changed from the original red-brown color of the extract to the dark purple

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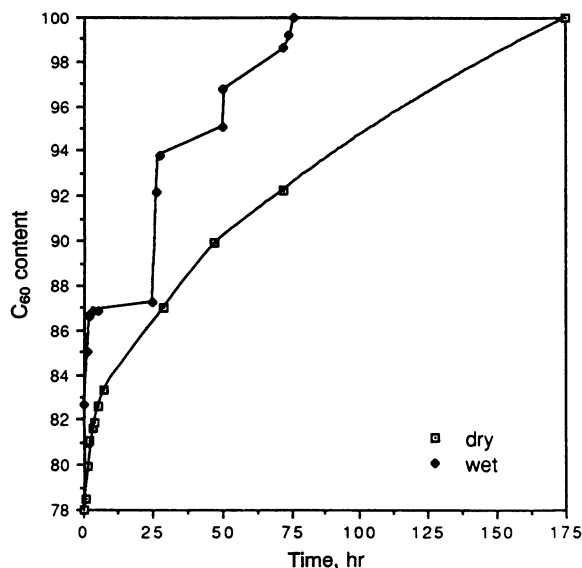


FIG. 2. C_{60} content vs. time under both dry and wet conditions.

color of C_{60} . The liquid phase composition was monitored by HPLC. The C_{60} content of the liquid phase plotted against time is shown in Fig. 2. The stepwise increase of the C_{60} content upon addition of each increment of water clearly demonstrates its effect on the complexation of C_{70} . The stepwise procedure took about 75 hr. However, upon addition of all the water in the initial stage of the procedure, the separation could be expedited (see above). Once the C_{60} content reached >99.8% as confirmed by HPLC (and verified by ^{13}C NMR), the liquid phase was decanted, neutralized with two 100-ml portions of saturated NaHCO_3 , washed with three 100-ml portions of water, and dried over 100 g of anhydrous MgSO_4 . The CS_2 was distilled off under reduced pressure and heat to give 1.20 g (73% recovery) of pure (>99.8%) C_{60} . Traces of the solvent remained trapped in the solid C_{60} unless it was heated under vacuum (250°C ; 0.1

mmHg). The C_{60} obtained did not show any contamination from $C_{60}\text{O}$ as analyzed by HPLC. To the remaining solid phase (mostly unreacted AlCl_3 and complexed C_{60} and C_{70}) 500 g of ice was added. The resulting sludge was first passed through a Buchner filter and then both the residue and the filtrate were extracted separately with 250 ml of CS_2 . After separation, the resulting CS_2 solutions were combined and treated similarly to the liquid phase containing C_{60} . Evaporation gave 0.42 g of C_{70} -enriched extract with a composition of 48% C_{60} and 52% C_{70} . HPLC chromatograms, shown in Fig. 3, illustrate the starting and resulting compositions. A similar procedure was used to separate 10.0 g of extract of identical initial composition, yielding 6.2 g (76% recovery) of pure C_{60} (>99.8%) and 1.9 g of a 1:1 C_{60}/C_{70} mixture. A total of 4.0 ml of water was added to 2000 ml of CS_2 solution of the extract during the first 3 hr. Although an aliquot taken after 24 hr and analyzed by HPLC showed the C_{60} content to be >99.8%, stirring was continued for another 24 hr before the two phases were separated. Vigorous mechanical stirring of the reaction mixture made it possible to use proportionally less AlCl_3 (130 g) than before.

We have attempted to characterize the Lewis acid adducts of C_{60} and C_{70} by NMR, IR, and UV spectroscopy. However, it has been difficult so far to conclusively demonstrate the nature of these complexes. The distinct jump in the differential complexation upon addition of each small (0.25-ml) increment of water indicates that the effective complexing agent may be the conjugate acid of AlCl_3 and not AlCl_3 itself. Both pure C_{60} and C_{70} when reacted with AlBr_3 (without deliberate addition of water) in CS_2 formed insoluble adducts, although at a substantially different rate. Other Lewis acids tried (neat or in solution) were SbF_5 , TiCl_4 , SnCl_4 , and FeCl_3 . No reaction was observed in neat SbF_5 at room temperature even after 5 months. Complexation did occur with all the weaker Lewis acids that were tried, but the efficiency was either low or both C_{60} and C_{70} behaved similarly. AlCl_3 is favored because it forms a heterogeneous system with the CS_2 solution of the fullerene extract and separation is thus easy.

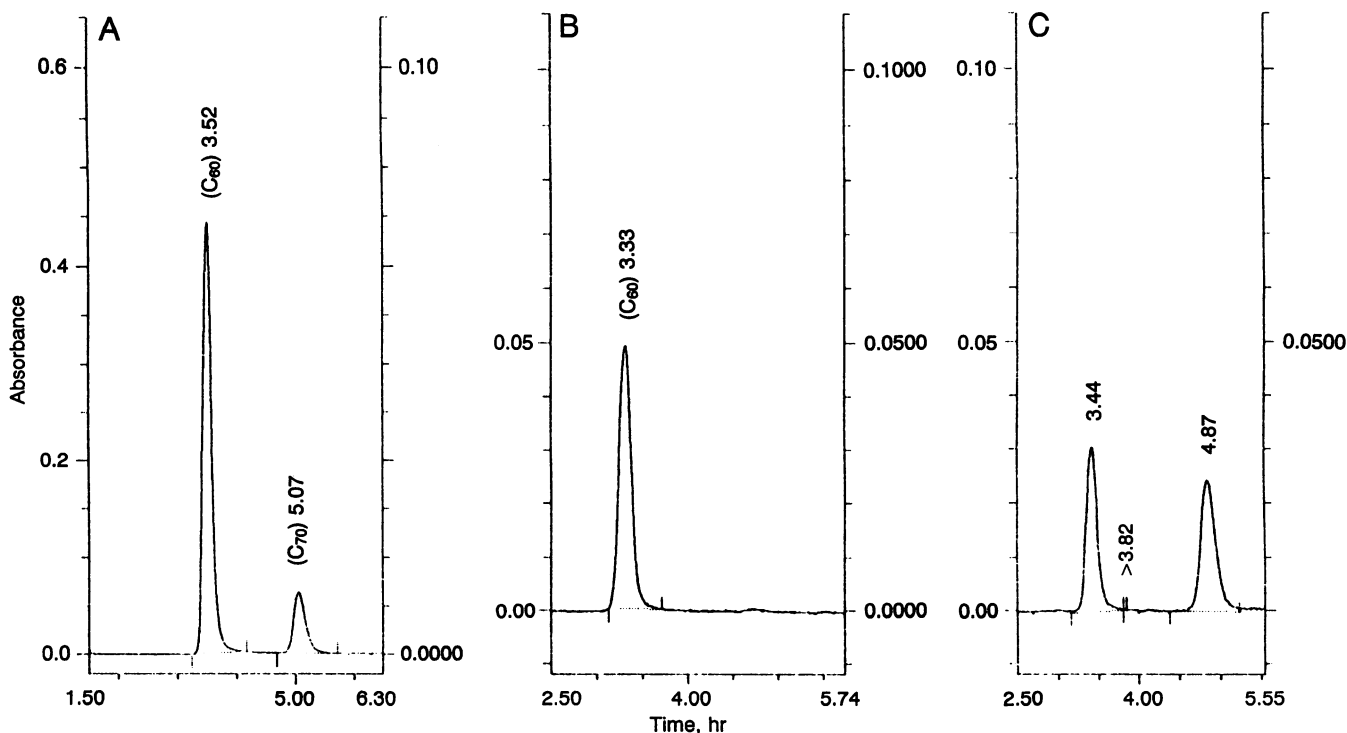


FIG. 3. HPLC traces. (A) Fullerene extract. (B) Purified C_{60} . (C) C_{70} -enriched residue.

In conclusion, based on selective complexation, we have developed a method for the multigram-scale separation of C₆₀ from higher fullerenes resulting in very-high-purity C₆₀ and with the use of only modest amount of solvent. A useful by-product of this separation is a C₇₀-enriched mixture of C₇₀ and C₆₀. The procedure described above can be easily scaled up.

This is paper 6 in the series "Considered Polycarbon Supercage Chemistry"; paper 5 is ref. 15. We thank Professor F. Wudl and his group for numerous helpful discussions. Support of our work by the National Institutes of Health and the Office of Naval Research is gratefully acknowledged.

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