Kilogram-scale [60]Fullerene Separation from a Fullerene Mixture: Selective Complexation of Fullerenes with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)

Koichi Nagata,* Eiji Dejima, Yasuharu Kikuchi, and Masahiko Hashiguchi
Engineering and Development Center, Frontier Carbon Corporation,
1-1 Kurosaki-Shiroishi, Yahatanishi-ku, Kitakyushu 806-0004

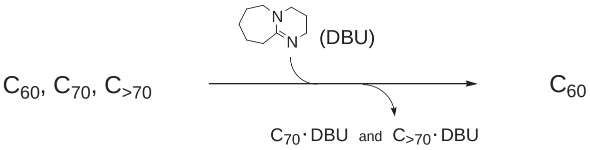
(Received October 4, 2004; CL-041169)

A very simple and efficient separation procedure for [60]fullerene from a fullerene mixture has been developed using the novel selective complexation of fullerenes with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). From 3.3 kg of the fullerene mixture, 1.35 kg of pure [60]fullerene was obtained.

In fullerene chemistry, the separation of [60]fullerene (C_{60}) from a fullerene mixture containing [70]fullerene (C_{70}) and higher fullerenes ($C_{>70}$) is important. Chromatographic methods[1,2] have been widely used to separate fullerenes. However, since they require large amounts of stationary and mobile phases, they are unsuitable for large-scale separations. Separations using host–guest interaction[3] are also commonly known. However these are used only for small-scale purifications because they require high-cost host compounds and involve complicated operations. In other words, a convenient industrial-scale [60]fullerene separation method does not exist, and the development of such a method is urgently required.

We now report a very simple and efficient procedure for separating one kilogram of [60]fullerene from a fullerene mixture using selective complexation with base including amidine structure (N=C–N), such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The procedure requires only conventional industrial unit operations, and can be easily scaled up to meet further demands.

When DBU was added to the fullerene extract containing C_{60}, C_{70}, and $C_{>70}$, black fullerene-DBU complex readily precipitated. We found that the ability of the complexation with DBU was in the order of $C_{>70} > C_{70} > C_{60}$ by HPLC analysis of the solution phase (Figure 1, left). Selective complexations of fullerenes with highly designed host compounds are commonly known.[3,4] However, our result is the first example of the selective complexation of higher fullerenes with a very simple amine.[5] We applied this complexation to the large-scale [60]fullerene separation (Scheme 1).



Scheme 1.

In a typical separation, fullerene mixture (3.3 kg, C_{60}: 57%, C_{70}: 24%, $C_{>70}$: 19%) was dissolved in 1,2,4-trimethylbenzene (TMB, 115 kg), to which DBU (3.3 kg) was added in 2 h with stirring at 0 °C under a nitrogen atmosphere. After 5 h, the purity of [60]fullerene in the solution phase reached >99% (Figure 1, right). The complex thus generated was removed by filtration, and the solution was washed with 0.2 mol/L HCl aq and water. [60]fullerene was then crystallized by adding MeOH, a poor solvent. The resulting precipitate was collected by filtration and dried under reduced pressure (200 °C, 1 mmHg) to give pure [60]fullerene (1.35 kg, purity: >99%, yield:[6] 72%). No DBU contamination in the product was detected by elemental analysis of nitrogen (<0.01%).

Among the various amines examined, DBU was found to be the best complexing agent, while 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 2-methyl-2-imidazoline can also be used. Notably, diamines such as 1,4-diazabicyclo[2.2.2]octane, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and *N*,*N*,*N*′,*N*′-tetraphenylethylenediamine as well as monoamines such as Et_3N and $Et(i\text{-}Pr)_2N$ gave no precipitates at all. These results suggest that the amidine structure (N=C–N) is indispensable for the present procedure. The fact that the complex formation also proceeds in the dark indicates that it is not a photo-induced radical reaction of fullerene with a tertiary amine.[7] Temperature is also an important factor. At a higher temperature, the complexation was inhibited in the present system, and the rate of complexation at 40 °C was approximately the half of that at 0 °C.

Hirsch et al. previously reported the formation of a 1:1 [60]fullerene/DBU complex.[8] From UV/VIS/NIR and ESR studies, they interpreted that the reaction undergoes in 2 steps. First, a single electron transfer from DBU to [60]fullerene occurs, and then a C–N covalent bond is formed upon a radical recombination process. Therefore, we speculate that the selective DBU-complexation of the higher fullerenes is related to the higher electron-affinity (EA) of these compounds[9] than to that of [60]fullerene (EA: 2.65 eV). As shown in Figure 2, the complexation of C_{76}, having comparatively lower EA (2.89 eV), was much slower than other higher fullerenes (C_{78}: 3.10 eV, C_{82}: 3.14 eV, C_{84}: 3.14 eV).[9] However, it is difficult to rationalize the selectivity toward C_{70} (2.73 eV) in terms of EAs alone. Although the difference in the EAs between C_{60} and C_{70}

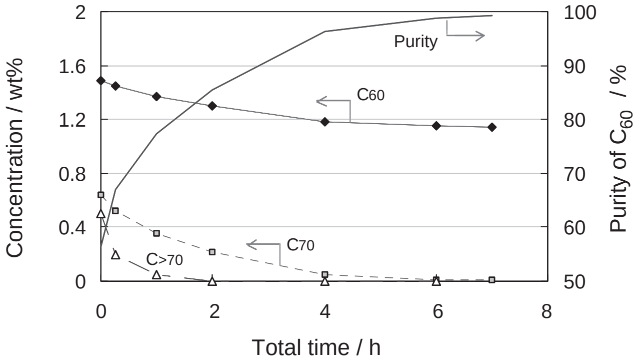


Figure 1. Concentration of C_{60}, C_{70}, and $C_{>70}$ (left) and purity of C_{60} (right) in the solution phase treated with DBU.

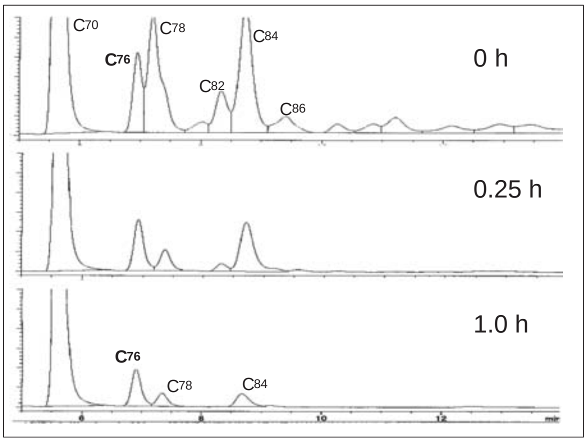


Figure 2. HPLC profiles of higher fullerenes in the solution phase at 308 nm.

(0.08 eV) was much smaller, the rate constant of C_{70} with DBU was about 10 times larger than that of C_{60}. It is necessary to consider other parameters such as the solubilities of the complexes and the curvatures of fullerenes. Further studies are required to distinguish the selective complexation mechanism.

On the other hand, the black precipitate formed during [60]fullerene separation is abundant in the valuable components: higher fullerenes.[10] Slight modifications make the present procedure a method of choice for large scale isolation of a higher fullerenes mixture. By reducing the amount of DBU to 1.0 kg using the above method, the higher fullerenes could be precipitated out in high selectivity. The precipitated complex was isolated by filtration, and decomplexed with AcOH in TMB to give 120 g of a highly $C_{>70}$-enriched fullerene mixture (C_{60}: 5%, C_{70}: 5%, $C_{>70}$: 90%). Based on the quantity in the initial mixture, 19% of higher fullerenes could be recovered. However, the complex is susceptible to air-oxidation, and therefore it needs to be handled in an inert atmosphere.

In summary, the simple and inexpensive procedure, which only uses commercially available materials, allows us to obtain [60]fullerene in industrial scale. Given the effectiveness of the separation procedure and the recent development of a 40 ton/year scale commercial production of the fullerene mixture,[11] we expect that [60]fullerene will be more easily available to both scientists and engineers.

We thank Prof. Eiichi Nakamura for helpful technical consulting. We are also grateful to Mitsubishi Chemical Science and Technology Research Center, Inc. for useful suggestion and discussion.

References and Notes

1 a) M. A. Wilson, L. S. K. Pang, and A. M. Vassallo, *Nature*, **355**, 117 (1992). b) W. A. Scrivens, P. V. Bedworth, and J. M. Tour, *J. Am. Chem. Soc.*, **114**, 7917 (1992). c) A. D. Darwish, H. W. Kroto, R. Taylor, and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, **1994**, 15. d) W. A. Scrivens, A. M. Cassell, B. L. North, and J. M. Tour, *J. Am. Chem. Soc.*, **116**, 6939 (1994).

2 Recently separation of fullerene by filtration through a thin layer of activated carbon has been reported. Although the volume of eluent could be reduced remarkably by the procedure, 42 mL of chlorobenzene was used for ca. 0.10 g of [60]fullerene separation.: N. Komatsu, T. Ohe, and K. Matsushige, *Carbon*, **42**, 163 (2004).

3 a) J. L. Atwood, G. A. Koutsantonis, and C. L. Raston, *Nature*, **368**, 229 (1994). b) T. Suzuki, K. Nakashima, and S. Shinkai, *Chem. Lett.*, **1994**, 699.

4 a) J.-Y. Zheng, K. Tashiro, Y. Hirabayashi, K. Kinbara, K. Saigo, T. Aida, S. Sakamoto, and K. Yamaguchi, *Angew. Chem., Int. Ed.*, **40**, 1858 (2001). b) Y. Shoji, K. Tashiro, and T. Aida, *J. Am. Chem. Soc.*, **126**, 6570 (2004).

5 Similar interaction of fullerenes and $AlCl_3$ in CS_2 has been reported. I. Bucsi, R. Aniszfeld, T. Shamma, G. K. Surya Prakash, and G. A. Olah, *Proc. Natl. Acad. Sci. U.S.A.*, **91**, 9019 (1994).

6 Based on the quantity of [60]fullerene in the starting material.

7 a) G. Schick, K.-D. Kampe, and A. Hirsch, *J. Chem. Soc., Chem. Commun.*, **1995**, 2023. b) G. E. Lawson, A. Kitaygorodskiy, B. Ma, C. E. Bunker, and Y.-P. Sun, *J. Chem. Soc., Chem. Commun.*, **1995**, 2225.

8 A. Skiebe, A. Hirsch, H. Klos, and B. Gotschy, *Chem. Phys. Lett.*, **220**, 138 (1994).

9 O. V. Boltalina, E. V. Dashkova, and L. N. Sidorov, *Chem. Phys. Lett.*, **256**, 253 (1996).

10 a) F. Diedrich, 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**, 548 (1991). b) F. Diedrich and R. L. Whetten, *Acc. Chem. Res.*, **25**, 119 (1992). c) C. Thilgen and F. Diederich, *Top. Curr. Chem.*, **199**, 135 (1999).

11 J.-F. Tremblay, *Chem. Eng. News*, **81** (32), 13 (2003). See also http://www.f-carbon.com

Published on the web (Advance View) January 8, 2005; DOI 10.1246/cl.2005.178