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Efficient and Scalable Method for [60]Fullerene Separation from a Fullerene Mixture: Selective Complexation of Fullerenes with DBU in the Presence of Water

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Abstract:

The acceleration effect of water in the selective complexation of fullerenes with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was investigated. Although selective complexation with DBU is useful for large-scale [60]fullerene separation from a fullerene mixture, the complexation is too slow for practical application at ambient temperature without the addition of water. In the presence of a small amount of water, the complexation accelerated considerably, and a pure [60]fullerene solution was readily obtained by complexation at 20 °C. The procedure was easily scaled up, and 1.3 kg of pure [60]fullerene was obtained from 3.0 kg of the fullerene mixture.

Introduction

Since their discovery in 1985,[1] fullerenes have attracted the interest of scientists and engineers because of their unique molecular structures. A large-scale facility that has a capacity to produce 40 metric tons of fullerenes per year has been operating since 2003.[2] In the fullerene family, [60]fullerene (C_{60}) in particular has been the subject of intense interest as a raw material for organic electronic devices and drugs because of its extremely high symmetry and reactivity. Since fullerenes are produced as a mixture containing [60]fullerene, [70]fullerene (C_{70}), and higher fullerenes ($C_{>70}$), the separation of [60]fullerene from other isomers is crucial. Two fundamental technologies are known for [60]fullerene purification: chromatography[3] and separation through the formation of inclusion complexes,[4] both of which can be modified to achieve effective separation on a laboratory scale. However, the former requires large amounts of stationary and mobile phases, and this procedure is difficult to scale up. The latter requires high-cost host compounds and involves intricate operations. Therefore, both methods are unsuitable for large-scale [60]fullerene separation.

Recently, we reported a novel [60]fullerene separation procedure using the selective complexation of fullerenes with DBU (Scheme 1).[5] The interaction between [60]fullerene and DBU was reported by Hirsch et al.,[6] and we believe that our method should be based on this interaction. This separation procedure requires only commercially available materials and conventional unit operations; therefore, it is suitable for large-scale [60]fullerene separation. However, the complexation rate is significantly slow at ambient temperature, and the fullerene solution has to be cooled to 0 °C to complete the complexation on a practical time scale. In this contribution, we report the acceleration effect of water in the complexation. In the presence of a small amount of water, the selective complexation accelerated considerably and was readily completed even at 20 °C. Since further cooling of the fullerene solution was not required, a more pragmatic procedure for [60]fullerene separation was achieved.

Results and Discussion

Selective Complexation of Fullerenes and DBU without Water.[5] When DBU is added to a fullerene mixture (C_{60}: 57%, C_{70}: 24%, $C_{>70}$: 19%) in 1,2,4-trimethylbenzene (TMB), a black fullerene−DBU complex readily precipitates. We found that the ability of complexation is in the order of $C_{>70} > C_{70} > C_{60}$, by HPLC analysis of the solution phase. The complexation was examined with various amines at 0 °C to carry out a detailed investigation. The fullerene components in the solution phase after 5 h complexation are summarized in Table 1. DBU was found to be the best complexing agent among the various amines examined, while DBN and 2-methyl-2-imidazoline can also be used. Notably, diamines such as DABCO and TMEDA as well as monoamines yielded no precipitates at all. These results suggest that the amidine structure (N═C−N) is indispensable for complexation. It is important to cool the fullerene solution to 0 °C. At a higher temperature, complexation was inhibited in the present system, and the rate of complexation at 40 °C was approximately half of that at 0 °C.

The formation of the 1:1 [60]fullerene/DBU complex was previously reported by Hirsch et al.[6] From spectra studies,

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Scheme 1

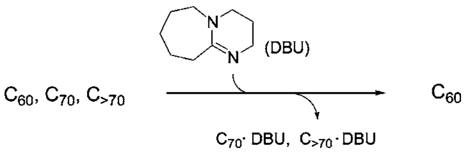

Table 1. **Complexation of fullerenes and various amines without water at 0°C**

entry	amine[a]	component (%) C_{60}	C_{70}	$C_{>70}$	C_{60} yield[b] (%)
1	DBU	>99	<1	0	72
2	DBN	>99	<1	0	70
3	2-Me-2-imidazolene	>99	<1	0	68
4	DABCO	57	24	19	100
5	TMEDA	57	24	19	99
6	Et_3N	57	24	19	100

[a] 6.9 mmol of amine was used for 1.0 g of fullerene mixture (C_{60}: 57%, C_{70}: 24%, $C_{>70}$: 19%). [b] Based on the quantity of [60]fullerene in the starting fullerene mixture.

Table 2. **Complexation of fullerenes and DBU in the presence of a small amount of water at 20 °C[a]**

entry	amount of H_2O (equiv of DBU)	component (%) C_{60}	C_{70}	$C_{>70}$	C_{60} yield[b] (%)
1	0	88	11	1	86
2	0.16	>99	<1	0	73
3	0.32	>99	<1	0	77
4	0.64	99	1	0	78
5	1.61	89	10	1	88

[a] 6.9 mmol of DBU was used for 1.0 g of fullerene mixture (C_{60}: 57%, C_{70}: 24%, $C_{>70}$: 19%). [b] Based on the quantity of [60]fullerene in the starting fullerene mixture.

they interpreted that the reaction proceeds in two steps. First, a single electron transfer from DBU to fullerene occurs; the complex ($[DBU]^{+}-[C_{60}]^{-}$) is then obtained via a radical recombination process. Therefore, we speculate that the selective complexation of higher fullerenes with DBU is related to the higher electron affinity of these compounds[7] than that of [60]fullerene.

Selective Complexation of Fullerenes and DBU in the Presence of a Small Amount of Water. In a series of experiments using various amines, we accidentally found that the complexation was highly accelerated in the presence of a small amount of water. Experiments for optimizing the amount of water were carried out using DBU as the base at 20 °C. The results are summarized in Table 2. At 20 °C, the purity of [60]fullerene in the solution reached only 88% without the addition of water. However, when 4% (w/w fullerene mixture) of water was added, the purity reached >99% in 5 h (entry 3). The amount of water corresponds to 0.32 equiv of DBU and 0.1 wt % of TMB. In addition, [60]fullerene was obtained in higher yield than that obtained at 0 °C without the addition of water (Table 1, entry 1).

As described in the previous section, the complex formed in the present system would have the zwitterion structure. We conjecture that the complexation was highly accelerated by water because of the highly polar nature of water that stabilized the polar transition state or the zwitterion complex. However, excess water showed no effect on the acceleration. We speculate that the excess water should hydrate DBU and prevent the complexation.

To investigate the additive effect in detail, complexation was carried out with some polar solvents as additives. Table 3 summarizes the results with the polarity parameters for the solvents:[8] the dielectric constant,[9] $E_T(30)$ polarity parameter,[10] and cohesive energy density.[11] Although water was found to be the best additive to accelerate the complexation, DMSO and DMF accelerated the complexation significantly, as expected. However, MeOH, which has a polarity similar to that of DMSO and DMF, did not accelerate the complexation. Therefore, to our knowledge, there exists no polarity parameter that completely explains the acceleration mechanism, and various acceleration mechanisms may exist for each solvent. Recently, the acceleration effect of DMSO in the reaction of [60]fullerene with a secondary amine was reported by Nakamura, Isobe et al.,[12] and they interpreted that DMSO must be stabilizing the ion pair of [60]fullerene anion radical and aminium radical. Similarly, in our case, it is certain that the polarity of a solvent helps the electron transfer and the following bond formation. Further studies are required to investigate the additive effect in detail.

Large-Scale [60]Fullerene Separation. A kilogram-scale [60]fullerene separation was executed to confirm the usefulness of the present separation procedure. At 20 °C, 3.0 kg of fullerene mixture was dissolved in TMB under nitrogen atmosphere, to which 0.12 kg of water was added. Then 3.1 kg of DBU was added. After 5 h, the purity of [60]fullerene reached >99%, and the suspension was treated to yield 1.3 kg of pure [60]fullerene (purity: >99%, yield:[13] 76%), as described below. No DBU contamination in the product was detected by the elemental analysis of nitrogen (<0.01%).

Experimental Section

The fullerene mixture was supplied by Frontier Carbon Corp. DBU was purchased from San-Apro. Other amines were supplied by Tokyo Kasei (TCI). 1,2,4-Trimethylbenzene (>99%) was purchased from Maruzen Chemicals. 2-Propanol was supplied by Tokuyama Corp. DMF, DMSO, and MeOH were purchased from Wako Chemical Co. These materials were used without further purification. HPLC was performed with an Agilent 1100 series chromatograph.

All experiments were performed under nitrogen atmosphere using glass reactors or a 300-L glass-lined reactor.

Procedure for the Complexation of Fullerenes and Various Amines without Water. The fullerene mixture (1.0

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(13) Based on the quantity of [60]fullerene in the starting fullerene mixture.

Table 3. **Complexation of fullerenes and DBU in the presence of a small amount of additive at 20°C**[a]

additive[b]	component (%)			yield[c] of C_{60} (%)	dielectric constant	E_T (kcal/mol)	cohesive energy density (cal/mol^3)
	C_{60}	C_{70}	$C_{>70}$				
none[d]	88	11	1	86	–	–	–
water[e]	>99	<1	0	77	78.39	63.1	550.2
DMSO	97	3	0	79	46.45	45.1	168.6
DMF	>99	<1	0	75	36.71	43.2	139.2
MeOH	89	10	1	88	32.66	55.4	208.8

[a] 6.9 mmol of DBU was used for 1.0 g of fullerene mixture (C_{60}: 57%, C_{70}: 24%, $C_{>70}$: 19%). [b] 0.32 equiv for DBU was added. [c] Based on the quantity of [60]fullerene in the starting fullerene mixture. [d] Same as entry 1 in Table 2. [e] Same as entry 3 in Table 2.

g, C_{60}: 57%, C_{70}: 24%, $C_{>70}$: 19%) was dissolved in 1,2,4-trimethylbenzene (TMB, 39.0 g) to which an amine (6.9 mmol, DBU: 1.05 g, DBN: 0.86 g, 2-methyl-2-imidazoline: 0.58 g, DABCO: 0.77 g, TMEDA: 0.80 g, Et_3N: 0.70 g) was added in 10 min at 0 °C under a nitrogen atmosphere. After 5 h, the generated complex was removed by filtration, and the complex was washed with TMB (3.0 g). The combined organic layer was washed with 0.2 mol/L AcOH and water; the yield and the purity of [60]fullerene were determined by HPLC analysis.

Procedure for the Complexation of Fullerenes and DBU in the Presence of a Small Amount of Water. The fullerene mixture (1.0 g, C_{60}: 57%, C_{70}: 24%, $C_{>70}$: 19%) was dissolved in 1,2,4-trimethylbenzene (39.0 g) to which the following amount of water (entry 1: none; entry 2: 20 mg, 1.1 mmol; entry 3: 40 mg, 2.2 mmol; entry 4: 80 mg, 4.4 mmol; entry 5: 200 mg, 11.1 mmol) was added at 20 °C under a nitrogen atmosphere. After stirring for 10 min, DBU (1.05 g, 6.9 mmol) was added in 10 min. After 5 h, the suspension was treated as described above. The yield and the purity of [60]fullerene were determined by HPLC analysis.

Procedure for the Complexation of Fullerenes and DBU in the Presence of a Small Amount of Additive. The fullerene mixture (1.0 g, C_{60}: 57%, C_{70}: 24%, $C_{>70}$: 19%) was dissolved in 1,2,4-trimethylbenzene (39.0 g) to which an additive (2.2 mmol, water: 40 mg, DMSO: 172 mg, DMF: 161 mg, MeOH: 70 mg) was added at 20 °C under a nitrogen atmosphere. After stirring for 10 min, DBU (1.05 g, 6.9 mmol) was added in 10 min. After 5 h, the suspension was treated as described above. The yield and the purity of [60]fullerene were determined by HPLC analysis.

Procedure for Large-Scale [60]Fullerene Separation. A fullerene mixture (3.0 kg, C_{60}: 57%, C_{70}: 24%, $C_{>70}$: 19%) was dissolved in 1,2,4-trimethylbenzene (TMB, 117 kg) to which water (0.12 kg, 0.67 mol) was added at 20 °C under a nitrogen atmosphere. After stirring for 30 min, DBU (3.1 kg, 20.4 mol) was added in 2 h. After 4 h, the purity of [60]fullerene reached >99%, and the generated complex was removed by filtration; the complex was washed with TMB (6.0 kg). The combined organic layer was washed with 0.2 mol/L AcOH (130 kg) and water, and concentrated to attain a concentration of 1.8 wt % for [60]fullerene. [60]Fullerene was crystallized by adding *i*-PrOH (165 kg), a poor solvent, and the resulting precipitate was collected by filtration and dried to yield 1.3 kg of pure [60]fullerene (purity: >99%, yield: 76%).

Conclusion

By the serendipitous discovery of the water effect, a more pragmatic [60]fullerene separation procedure can be achieved by using selective fullerene–DBU complexation. Compared to the conventional methods, our method is efficient, low-cost, and can be easily scaled up because the separation procedure requires only mild conditions such as ambient temperature, commercially available materials, and conventional unit operations. We anticipate that the separation method will contribute to future developments in the field of fullerene science and technology.

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