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Facile Purification of $C_{60}O$-Containing [60]Fullerene Using Trialkylphosphines at Room Temperature

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ABSTRACT: A novel method using trialkylphosphines is reported for the facile purification of [60]fullerene containing $C_{60}O$. When tri-*n*-butylphosphine and tri-*n*-octylphosphine were added to unrefined C_{60} (ca. 97% purity) in 1,2,4-trimethylbenzene, $C_{60}O$ was readily reduced to give high-purity C_{60} (>99% purity). The best results were obtained for a high concentration (>1.0 wt %) of unrefined fullerene treated with tri-*n*-octylphosphine at room temperature. This method is simple and fast in comparison with conventional alumina chromatography, and thus, it is well-suited to industrial-scale separation.

INTRODUCTION

High-purity fullerenes (C_{60}) are widely used in various fields, including medicine, materials science, and electronics. Thus far, several low-cost methods have been developed for the production[1] and purification[2] of parent fullerenes. We have reported a simple, low-cost method using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[3] to purify fullerenes. Fullerene mixtures can be produced by combustion synthesis.[4] However, fullerene oxides,[5] impurities typified by $C_{60}O$, are present in minute amounts in these mixtures. In addition, fullerene oxides are produced by photoreaction[6] and heating[6b,7] in the presence of oxygen, by electrochemical oxidation[8] using oxidants,[9,10] and by ozonolysis.[11] In many applications, low levels of impurities (<3%) produced by combustion synthesis have little or no effect on the performance of C_{60}. In organic photovoltaic cells, however, fullerene oxides sometimes lower power conversion efficiency.[12]

Our DBU-based purification method is not effective for removing small amounts of $C_{60}O$, and attempts to remove $C_{60}O$ from C_{60} by silica gel chromatography[13] have been unsuccessful. At present, neutral alumina is commonly used as an adsorbent for $C_{60}O$; however, alumina chromatography is an expensive and laborious procedure because it requires large quantities of alumina and solvents.[6b] Although it has been reported that $C_{70}O$ is reduced to C_{70} by the addition of large amounts of triphenylphosphine, the reaction is slow and cannot be used in the industrial purification of fullerenes.[14] Therefore, an efficient, low-cost, and facile procedure for removing fullerene oxides from parent fullerenes is needed.

Herein, we report a new method using trialkylphosphines to purify [60]fullerene containing $C_{60}O$. We found that trialkylphosphines—tri-*n*-butylphosphine and tri-*n*-octylphosphine—reduced $C_{60}O$ more readily and effectively than triphenylphosphine (for structures, see Figure 1). Our method is simple, as it involves only combining fullerene and trialkylphosphine, recrystallization, and filtration. Via this method, C_{60} with 99.9% purity can be obtained from unrefined C_{60} (approximately 97% purity). Further, it is particularly worth noting that our method is more effective than conventional alumina chromatography for the industrial purification of fullerenes.

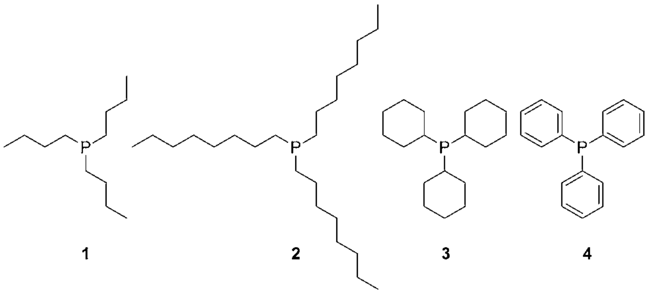

Figure 1. Trialkylphosphines (**1**, **2**, and **3**) and triphenylphosphine (**4**).

RESULTS AND DISCUSSION

When a trialkylphosphine was added to $C_{60}O$-containing [60]fullerene (C_{60}, 97%; $C_{60}O$, 3%) in 1,2,4-trimethylbenzene, $C_{60}O$ was readily reduced to C_{60}. The HPLC analysis results shown in Figure 3 indicate that **2** was effective in the purification of C_{60}. Even in small amounts (2 equiv with respect to $C_{60}O$), **1** and **2** were able to rapidly reduce $C_{60}O$. However, in the case of **3**, a large excess and a long reaction time were required to remove $C_{60}O$. When **4** was used, all of the $C_{60}O$ could not be removed (Table 1, Figure 4). We surmise that steric hindrance influences the reactivity for reduction of $C_{60}O$.

The proposed reaction mechanism for the method is shown in Scheme 1. First, a covalent bond is formed between the phosphorus atom of trialkylphosphine and an oxygen atom of $C_{60}O$ via epoxide ring-opening. The fullerene anion thus

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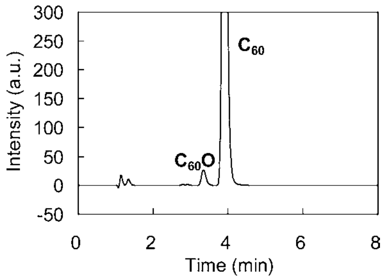


Figure 2. HPLC profile of unrefined [60]fullerene (C_{60}, 97; $C_{60}O$, 3%). Conditions: YMC-Pack ODS-AM; particle size, 3 μm; i.d., 4.6 mm × 75 mm; eluent, methanol/toluene = 6/4; flow rate, 1.0 mL/min.

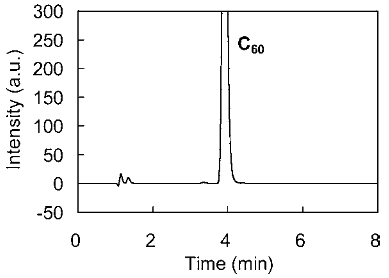


Figure 3. HPLC profile of [60]fullerene (C_{60}: 99.9%) by purified using tri-*n*-octylphosphine (**2**). Conditions: YMC-Pack ODS-AM; particle size:, 3 μm; i.d., 4.6 mm × 75 mm; eluent, methanol/toluene = 6/4; flow rate, 1.0 mL/min.

Table 1. Purity of $C_{60}O$-Containing [60]Fullerene Obtained by Using Various Phosphines

entry	phosphine compound	equiv[a]	temp (°C)	time	component (area %)	
					C_{60}	$C_{60}O$
1	none				97.0	3.0
2	**1**	2	25	1 h	99.7	<0.01
3	**1**	2	40	1 h	99.8	<0.01
4	**1**	2	70	1 h	99.8	<0.01
5	**1**	2	100	1 h	99.5	<0.01
6	**2**	2	25	1 h	99.9	<0.01
7	**2**	2	40	1 h	99.9	<0.01
8	**2**	2	70	1 h	99.9	<0.01
9	**2**	2	100	1 h	99.8	<0.01
10	**3**	2	25	4 h	96.9	3.0
11	**3**	60	25	4 h	98.8	1.1
12	**4**	60	25	4 h	96.8	2.9
13	**4**	60	70	4 h	97.3	2.5
14	**4**	60	100	4 h	98.3	1.6

[a] With respect to $C_{60}O$.

generated is immediately converted to C_{60} by elimination of trialkylphosphine oxide.

Trialkylphosphine oxide, which dissolves well in 1,2,4-trimethylbenzene and 2-propanol, can be easily removed by recrystallization of C_{60}. The C_{60}/trialkylphosphine oxide mixture was first dissolved in 1,2,4-trimethylbenzene, and then C_{60} was recrystallized by adding 2-propanol as a poor solvent at 40 °C. The resulting precipitate was collected by filtration and dried under reduced pressure (100 °C, 1 mmHg) to yield high-purity C_{60} (up to 99.9%). X-ray photoelectron spectroscopy (XPS) showed that the product contained <10 ppm of phosphorous contaminants.

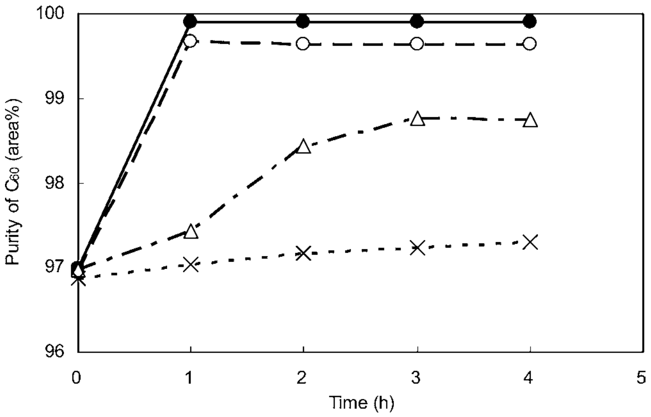
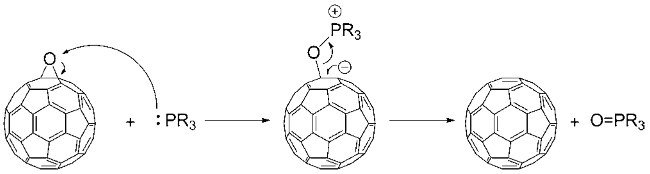


Figure 4. Purity of C_{60} obtained by treating $C_{60}O$-containing [60]fullerene with various phosphines at 25 °C. **1**: trin-butylphosphine, 2.0 equiv (open circle); **2**: tri-*n*-octylphosphine, 2.0 equiv (solid circle); **3**: tricyclohexylphosphine, 60 equiv (open triangle); **4**: triphenylphosphine, 60 equiv (cross).

Scheme 1. Proposed Reaction Mechanism



Next, we investigated the optimal reaction conditions for our purification method. The purity of C_{60} obtained by this method at temperatures ranging from 25 to 100 °C is shown in Figure 5. Among the three phosphines, **2** provided the best results. Unidentifiable impurities were produced at high temperatures via a side reaction in which C_{60} reacted with the trialkylphosphine oxide, as previously reported by Wu et al.[15] Therefore, the most favorable temperature was found to be 25 °C. Figure 6 shows the purity of C_{60} obtained by using **1** at various fullerene concentrations, and it was confirmed that a high concentration (>1.0 wt %) of fullerenes is favorable for the proposed method. In addition, we tested other aromatic organic solvents such as toluene and xylene instead of 1,2,4-trimethylbenzene. These solvents gave similar results. However,

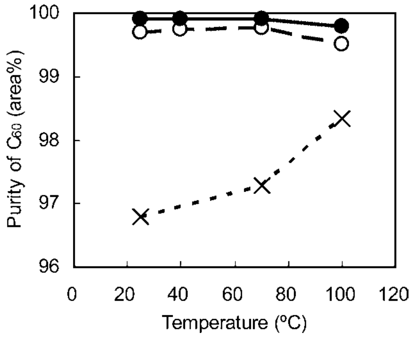


Figure 5. Purity of C_{60} obtained from $C_{60}O$-containing [60]fullerene at various temperatures. **1**: tri-*n*-butylphosphine, 2.0 equiv (open circles); **2**: tri-*n*-octylphosphine, 2.0 equiv (solid circles); **4**: triphenylphosphine, 60 equiv (crosses).

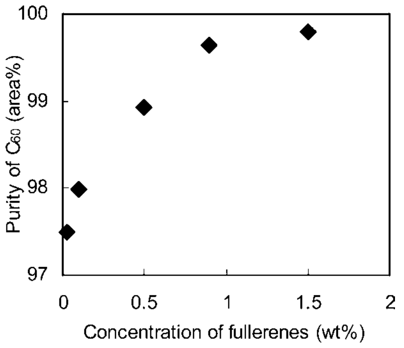


Figure 6. Purity of C_{60} obtained from $C_{60}O$-containing [60]fullerene of various concentrations by using tri*n*-butylphosphine **1** (2.0 equiv).

from the viewpoint of solubility, 1,2,4-trimethylbenzene was most suitable for this purification method.

EXPERIMENTAL SECTION

Methods and Materials. Trialkylphosphines—tri-*n*-butylphosphine (**1**), tri-*n*-octylphosphine (**2**), and tricyclohexylphosphine (**3**)—and triphenylphosphine (**4**) (Figure 1) were used for the experiment. An unrefined $C_{60}O$-containing [60]fullerene (C_{60}, 97%; $C_{60}O$, 3%) sample was supplied by Frontier Carbon Corporation. **1**, **2**, and **4** were purchased from Tokyo Chemical Industry Corporation, and **3** was purchased from Sigma-Aldrich Corporation. 1,2,4-Trimethylbenzene and 2-propanol were purchased from Wako Pure Chemical Industries and used as received. The sample was produced by the combustion synthesis method, and it mainly contained the desired C_{60} and small amounts of fullerene oxides (composed mostly of $C_{60}O$, as indicated by the HPLC results shown in Figure 2).

All the reactions were carried out under a nitrogen atmosphere, and the resulting products were analyzed by reversed-phase HPLC (column, YMC-Pack ODS-AM; particle size, 3 μm; i.d., 4.6 mm × 75 mm; flow rate, 1.0 mL/min; eluent, methanol/toluene = 6/4; detection wavelength, 290 nm).

Purification Using Tri-*n*-butylphosphine (1). $C_{60}O$-containing [60]fullerene (2.01 g; 2.79 mmol; C_{60}, 97%; $C_{60}O$, 3%) was dissolved in 1,2,4-trimethylbenzene (150 mL) to which **1** (34 mg, 0.17 mmol) was added by stirring at 25 °C for 1 min under a nitrogen atmosphere. After 1 h, the purity of C_{60} was >99%. Insoluble impurities were removed by filtration. C_{60} was crystallized by adding 2-propanol (600 mL) as a poor solvent at 40 °C, and the resulting precipitate was collected by filtration and dried under reduced pressure (100 °C, 1 mmHg) to yield 1.88 g of pure C_{60} (purity, 99.7%; yield, 94%).

Purification Using Tri-*n*-octylphosphine (2). $C_{60}O$-containing [60]fullerene (2.00 g; 2.78 mmol; C_{60}, 97%; $C_{60}O$, 3%) was dissolved in 1,2,4-trimethylbenzene (150 mL) to which **2** (62 mg, 0.17 mmol) was added by stirring at 25 °C for 1 min under a nitrogen atmosphere. After 1 h, the purity of C_{60} was >99% (Figure 3). Insoluble impurities were removed by filtration. C_{60} was crystallized by adding 2-propanol (600 mL) as a poor solvent at 40 °C, and the resulting precipitate was collected by filtration and dried under reduced pressure (100 °C, 1 mmHg) to yield 1.85 g of pure C_{60} (purity, 99.9%; yield, 93%).

Purification Using Tricyclohexylphosphine (3). $C_{60}O$-containing [60]fullerene (2.00 g; 2.78 mmol; C_{60}, 97%; $C_{60}O$, 3%) was dissolved in 1,2,4-trimethylbenzene (150 mL) to which **3** (1.40 g, 5.0 mmol) was added by stirring at 25 °C for 1 min under a nitrogen atmosphere. After 4 h, the purity of C_{60} was >98%. Insoluble impurities were removed by filtration. C_{60} was crystallized by adding 2-propanol (600 mL) as a poor solvent at 40 °C, and the resulting precipitate was collected by filtration and dried under reduced pressure (100 °C, 1 mmHg) to yield 1.87 g of pure C_{60} (purity, 98.8%; yield, 94%).

Purification Using Triphenylphosphine (4). $C_{60}O$-containing [60]fullerene (2.02 g; 2.80 mmol; C_{60}, 97%; $C_{60}O$, 3%) was dissolved in 1,2,4-trimethylbenzene (150 mL) to which **4** (1.31 g, 5.0 mmol) was added by stirring at 100 °C for 1 min under a nitrogen atmosphere. After 4 h, the purity of C_{60} was >98%. Insoluble impurities were removed by filtration. C_{60} was crystallized by adding 2-propanol (600 mL) as a poor solvent at 40 °C, and the resulting precipitate was collected by filtration and dried under reduced pressure (100 °C, 1 mmHg) to yield 1.82 g of pure C_{60} (purity, 98.3%; yield, 90%).

CONCLUSION

We have developed a facile purification method that reduces [60]fullerene containing $C_{60}O$ to obtain high-purity C_{60} (up to 99.9%) at room temperature. The effective reduction of $C_{60}O$ using trialkylphosphines such as tri-*n*-butylphosphine and tri-*n*-octylphosphine provides a pragmatic [60]fullerene purification method. We determined the optimal reaction conditions for this method. Furthermore, experimental results showed that, as compared to the conventional chromatography method, the present method is facile, efficient, and easy to scale up. Thus, this method can be used for industrial-scale separation. We believe that our purification method will contribute greatly to future developments in the field of fullerene science and technology.

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Notes

The authors declare no competing financial interest.

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