

Significant promotional effect of CCl₄ on fullerene yield in the graphite arc-discharge reaction†

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Addition of a small quantity (~3%) of CCl₄ to the He atmosphere of the graphite arc-discharge reaction revealed a marked increase in fullerene yield.

Since macroscopic quantities of C₆₀ and other fullerenes were prepared by the method of graphite arc-discharge in a He atmosphere by Krätschmer and Huffman in 1990,¹ various alternative methods have been reported to produce fullerenes. These include incomplete combustion of benzene or hydrocarbons² (the combustion method has now been extended to large scale fullerene production by the Mitsubishi Corporation),³ pyrolysis of naphthalene,⁴ and dissociation of hydrocarbons in thermal plasma.^{5,6} However, arc-discharge between graphite rods under a low-pressure of inert-gas remains one of the most efficient processes.

In the past decade, great efforts have been focused on optimizing reaction conditions in graphite arc-discharge for fullerene preparation. Variations include the type and pressure of foreign gases,^{7,8} the shape and composition of graphite electrodes,^{9,10} and the reaction temperature.^{11,12} In previous reports,^{13–15} fullerene C₆₀ can be synthesized in relatively good yield (*e.g.* up to 15% or more under optimal reaction conditions). The cost of fullerenes by this method, however, is still prohibitively expensive for industrial applications. Therefore, simpler and more efficient methodology must be found to reduce the cost. We now report that a small amount of CCl₄

mixed into He atmosphere remarkably enhances the fullerene formation in the graphite arc-discharge reaction. This finding will be of significance for large scale fullerene synthesis, and provides valuable clues to the investigation of the mechanism of fullerene formation.

In the present experiment, graphite arc-discharge was performed under an atmosphere of He, CCl₄, or mixtures thereof. The setup (see ESI)† includes a stainless steel cylinder reactor (30 cm I.D. × 50 cm) equipped with two graphite electrodes: a block of graphite (cathode, with a diameter of 130 mm and a thickness of 15 mm) and a graphite rod (anode, 6 mm in diameter and 15 cm in length). After discharge reaction at 24 V and 100 A for half an hour, about 3–4 g of soot was produced. In each run, 2.7 g was collected for extraction with 150 ml toluene in a Soxhlet extractor. To study the effects of the He/CCl₄ medium and pressure on fullerene production, the toluene-soluble extract was condensed to 25 ml for examination of the product by reverse phase liquid chromatography and ultraviolet spectrometry (LC-UV) using a TSP Model P2000 HPLC coupled with a TSP UV3000 detector. Analysis focused on the relative yields of C₆₀ and C₇₀ versus consumed graphite reactant, estimated from their peak areas in the HPLC-UV chromatograms of the toluene-soluble products detected at 330 nm. A chromatographic example and the linear correlation plots of peak areas against fullerene concentrations are shown in the ESI† The fullerene yields (C₆₀ and C₇₀) under various reaction conditions, and peak areas, as well as the amounts of consumed graphite reactant and collected soot product, are listed in Table 1.

Among the many reports regarding fullerene synthesis by graphite arc-discharge with different foreign gas additives (He, Ar, N₂, Cl₂, C₂N₂ and CH₃OH *etc.*), a He atmosphere has been

† Electronic supplementary information (ESI) available: diagram of the experimental setup used; linear correlation plots of chromatographic peak area vs. fullerene concentration (C₆₀ and C₇₀); typical HPLC-UV chromatogram of the products; data for four repeats of experiments 4 and 5. See <http://www.rsc.org/suppdata/cc/b3/b306921b/>

Table 1 Fullerene yields in different CCl₄/He atmospheres

Experiment no.	Experimental conditions		Consumed graphite reactant/g	Collected soot/g	Chromatographic peak areas (mA.U. × min)		Fullerene weights in 2.7 g soot/mg		Fullerenes yields ^a (%)	
	CCl ₄ /Torr	He/Torr			C ₆₀	C ₇₀	C ₆₀	C ₇₀	C ₆₀	C ₇₀
1	0	0	3.53	3.40	<4	<4	<0.6	<0.3	<0.02	<0.01
2	0	40	3.24	3.13	<4	<4	<0.6	<0.3	<0.02	<0.01
3	0	80	2.90	2.89	<4	<4	<0.6	<0.3	<0.02	<0.01
4	0	300	2.80	2.78	465	119	73.2	9.6	2.7	0.4
5	10	300	1.45	2.70	1224	318	192.7	25.7	13.3	1.8
6	20	300	1.79	3.33	757	168	119.2	13.6	8.2	0.9
7	40	300	1.88	3.76	481	146	75.7	11.8	5.6	0.9
8	130	0	1.93	4.00	<4	<4	<0.6	<0.3	<0.05	<0.02
9	40	0	1.50	3.44	31	12	4.9	1.0	0.4	0.1
10	40	40	0.82	2.74	48	29	7.6	2.3	1.0	0.3
11	40	70	1.11	2.80	175	52	27.6	4.2	2.6	0.4
12	40	170	1.30	2.94	216	81	34.0	6.5	2.8	0.5
13	40	210	1.59	3.15	289	107	45.5	8.6	3.3	0.6

^a The fullerene yields are calculated by dividing the grams of fullerenes (C₆₀, C₇₀) obtained by the grams of graphite consumed. It is difficult to calculate the actual conversion of fullerenes from the total carbon sources (*i.e.* the carbon from both the graphite and the CCl₄ consumed), because the grams of the consumed CCl₄ cannot be determined exactly in the present experiments. The carbon source from the CCl₄, however, is deduced to be very little. As an example, 1.45 g of graphite was consumed but 2.70 g of soot was produced in Experiment no. 5. The obtained soot was 1.25 g more than the consumed graphite, and this extra mass was reasonably supposed to come from the CCl₄. Among the 1.25 g consumed CCl₄, only 0.097 g carbon might become the source for fullerenes, this weight is much lighter than the consumed graphite (1.45 g). Therefore, the fullerene conversion from both the graphite and CCl₄ consumed may be approximatively replaced by the fullerenes yield as listed here.

confirmed to be the best medium to promote fullerene formation.^{7–15} In agreement with the previous investigations, the fullerene yields in our reactor were optimized at a He pressure of about 300 Torr; the yield rapidly decreased on either increasing or decreasing the He pressure. It should be noted that the setup employed for the present experiments was not the most favorable one for fullerene production, and the yield of C₆₀ and C₇₀ from graphite arc-discharge in ambient He were determined to be less than those previously reported.^{13–15} The addition of CCl₄, however, brings our inferior fullerene generator up to the equal of the best previously reported C₆₀ generators. As shown in the HPLC-UV chromatogram in the ESI,[†] fullerenes as well as various chlorinated carbon clusters (CCCs), such as C₆Cl₆, C₁₀Cl₈, C₁₂Cl₈, C₁₄Cl₈, C₁₆Cl₁₀ and C₆₀Cl₈, were produced from the graphite arc-discharge reactions in the presence of CCl₄. The latter CCCs were similar to those obtained in the studies of chloroform glow discharge^{16,17} and microwave plasma.⁶ The structures of some CCCs were determined from their molecular formulae coupled with the characteristic retention times of reference compounds identified in previous studies.¹⁸ In the present studies they were not determined quantitatively. As indicated in Table 1, spectacular enhancements of fullerene yields were obtained when a small partial pressure of CCl₄ (10 Torr) was present (experiments 4 and 5). The repeatability in the proposed process was shown to be reasonable (see table in ESI,[†] where data for four repeats of experiments 4 and 5 are shown). Surprisingly, on sequentially increasing the partial pressure of CCl₄ to 20 and 40 Torr, the fullerene yields declined rapidly (experiments 5–7), while the total yield of CCCs increased concurrently. It was also revealing that when the graphite arc-discharge was run in a pure atmosphere of CCl₄ at 130 Torr (experiment 8), only CCCs and very little fullerenes were detected. It could be expected that fullerenes might thoroughly dominate over the products and CCC yields could be reduced to nearly zero when decreasing the CCl₄ partial pressure to a narrow value. This would remove the need for the purification of fullerenes from the CCCs mixture and prevent the fullerene generator from eroding in superfluous chlorinated species.

Existing investigations suggest that evaporated carbon clusters in the arc-discharge have free valences. These reactive intermediates have long lifetimes to grow to fullerenes (inert media with hot carbon atoms). Addition of some foreign species such as hydrogen or halogen, however, causes the free valences to be saturated and influences fullerene growth. Comparing different reactant sources including CH₄, C₂H₂, CBrF₃, CCl₂F₂, and C₂Cl₄, Alexakis and coworker's experiment in a thermal plasma showed that chlorine was a suitable species to increase fullerene yield.⁵ Further evidence in support of this conclusion comes from Scott's direct preparation of fullerene C₆₀ by heating a chlorinated hydrocarbon.¹⁹ The pyrolysis also worked without the chlorines but the yields were lower. Our studies suggest that the nascent state carbon clusters reversibly react with chlorine sources, e.g. CCl₄ or other chlorinated species, to afford CCCs, whereby the carbon cluster lifetimes are prolonged, and in turn the chance of fullerene formation is enhanced. Under the discharge conditions, equilibrium between carbon clusters and CCCs is established depending on the concentration of CCl₄. When the concentration of CCl₄ was too high, the bonding/dissociation equilibrium would be shifted,²⁰ most fullerene precursors would be stabilized, and growth of small carbon clusters would be stopped before they reach fullerenes. This proposal satisfactorily explains the high yields of fullerene in a low pressure of CCl₄ (10 Torr, experiment 5), the fullerene yields lower as the CCl₄ pressure increases. In addition, Table 1 shows not only the increase in fullerene yield but also an interesting change on the yield ratio of C₆₀ to C₇₀. For instance, the C₆₀/C₇₀ yield ratios are 7.7, 7.4, 9.1 and 6.2 in experiments 4, 5, 6, and 7, respectively. The fact that the ratio is changing contradicts the 85 : 15 ratio of C₆₀/C₇₀ in the traditional arc-discharge method, and lends credence to the hypotheses that reactive free-valence fullerene-growth inter-

mediates are stabilized in some way. Accordingly, we believe that trapping the fullerene intermediates (*i.e.* the CCCs) in the reaction and estimating the relationship between yields of CCCs and fullerenes could be of significance for investigation of the fullerene formation mechanism.

To test the cooperative effect of CCl₄ and He, the former was held at 40 Torr and the effect on the fullerene yield was studied by varying the He partial pressure. As shown in experiments 9–13, the yields increased steadily as He partial pressure was increased from 0 to 210 Torr. Together with experiment 7, these demonstrated the cooperative effect of CCl₄ and He on the fullerene formation process.

In conclusion, while the yields of fullerenes from our inferior reactor are only comparable to those obtained in the best fullerene generator previously reported,^{12–14} the major finding that the enhancement of fullerene formation *via* the addition of CCl₄ would not only be helpful for the mechanistic investigation of fullerenes but also amenable to practical preparation of fullerenes. It could be expected that the addition of a small quantity of CCl₄ to the optimal fullerene generator might significantly increase the best fullerene yields previously reported^{13–15} to some extent.

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