

The graphite arc-discharge in the presence of CCl_4 : Chlorinated carbon clusters in relation with fullerenes formation

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Abstract

The graphite arc-discharge in the atmosphere consisting of CCl_4 40 Torr and increasing partial pressure of He from 0 to 300 Torr produced, in addition to carbon species such as graphite and fullerenes C_{60} and C_{70} , numerous chlorinated carbon clusters (CCCs). The yields of some CCCs, including C_6Cl_6 (perchlorobenzene), C_{10}Cl_8 (perchloronaphthalene), C_{12}Cl_8 (perchloroacenaphthylene) and C_{12}Cl_8 (isomer II), C_{14}Cl_8 (isomer I), $\text{C}_{16}\text{Cl}_{10}$ (perchlorofluoranthene), $\text{C}_{18}\text{Cl}_{10}$ (isomer I and II), and $\text{C}_{20}\text{Cl}_{10}$ (isomer I), correspond well with C_{60} yields, which may imply these CCCs share the same growth mechanism with fullerenes. Such a yield correlation can be used to distinguish the fullerene precursors from the irrelevant by-products, thus contributes to the mechanistic study of fullerene formation.

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1. Introduction

While the fullerene preparation by Krätschmer's method (i.e. graphite arc-discharge in He atmosphere) [1] has been commercially applied for many years, the formation mechanism for such kind of caged carbon clusters is still not well understood owing to the lack of viable evidences [2–12], notably the lack of the information on possible intermediates. Upon this process was established, efforts were primarily directed to support the interpretations proposed by pioneers that see a number of attempts [13–17] to trap intermediates for the fullerene formation by the addition of various agents to the inert gas buffer medium. For instance, (i) the addition of cyanogen to the reaction medium results in polyene rods capped by cyano groups [13,14], (ii) that of either propene or methanol produces a

series of polycyclic aromatic hydrocarbons (PAHs) such as C_{12}H_8 , C_nH_{10} ($n = 14–18$) and C_nH_{12} ($n = 20, 22, 24$) [15], and (iii) that of chlorine species generates a number of chlorinated PAHs [13,16,17]. While these experiments provided excellent information for understanding the mechanistic details on the fullerene formation, the investigations have been stymied because an authentic relationship between trapped compounds and fullerenes could not be established [3]. In fact, the cited trapped compounds [13–17] were a complex mixture of a wide range of products that could be considered as intermediates for different end products such as fullerenes, carbon nanotubes and graphite etc. A challenge at this stage is to identify the trapped compounds and explore their relationship with fullerenes and, further, distinguish the authentic fullerenes intermediates among the vast number of products. Based on the yield correlation of fullerenes and their intermediates, we have discovered a novel variation pattern which may be used to distinguish the fullerene precursors from the irrelevant side-products. We wish to report the correlation trends and propose a relationship to the fullerene formation.

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2. Experimental

The graphite arc-discharge was performed in a stainless steel cylinder reactor equipped with two graphite electrodes: a block of graphite (cathode, with diameter of 130 mm and thickness of 15 mm) and a graphite rod (anode, with 6 mm I.D. and 15 cm in length). Before the discharge reaction, the chamber was evacuated to a pressure of ca. 10^{-2} Torr using a rotary pump, and then filled with CCl_4 vapor at the partial pressure of 40 Torr and He at appropriate pressure (we performed 12 experiments with 12 different He partial pressures ranging for 0 to 300 Torr). Discharge was observed between the gap of the two electrodes when an electrical source (24 V and 100 A) was supplied.

After discharge reaction for half an hour, about 3 g soot was produced, and 0.9 g soot was weighed out for extraction with 100 ml toluene in a Soxhlet extractor for 9 hour. The toluene solution was concentrated to 8 ml, followed by filtration through a $0.45 \mu\text{m}$ pore membrane to obtain a solution for high-performance liquid chromatography combined with mass spectrometry (HPLC-MS) analysis.

The instrument used for the HPLC-MS analysis was a TSP Model P2000 HPLC and a Finnigan LCQ mass spectrometer equipped with atmospheric pressure chemical ionization (APCI) interface. The APCI-MS analytic conditions have been previously described [18]. To fully isolate the compounds in the product, the HPLC separation was alternately performed under two sets of chromatographic conditions as follows: **(A)** Discovery C18 column ($250 \times 4.6 \text{ mm}$) of SUPELCO was used, and a gradient solvent mixture of methanol/ethanol/cyclohexane consisting of a linear increase in cyclohexane concentration from 0 to 5% in 50 min and from 5% to 35% in the next 200 min, against a linear decrease in methanol from 84.6% to 80.4% in 50 min and from 80.4% to 55% in the next 200 min, was used as eluent at a flow rate of 1.0 ml/min. **(B)** 2,4,6-trinitrophenol-modified zirconia-alumina column ($150 \times 4.6 \text{ mm}$) [19,20] was employed, and a toluene-cyclohexane eluent was flowed in 0.5 ml/min in a gradient mode: 100% cyclohexane eluted in the first 20 min and reduced to 70% in the next 40 min, then kept 20 min. The former HPLC procedure (i.e. condition **A**) was suitable for the separation of the chlorinated carbon clusters (CCCs) with lower molecular weight, while the later one was effective for larger CCCs and fullerenes [19,20]. The injection volume for the sample was $5 \mu\text{l}$.

The yield of each component separated in the HPLC-MS experiment could be estimated from the corresponding peak area according to the proportion relationship between peak area and its concentration in analyte solution. The relative standard deviation (RSD) for the peak area determination in the experiment was about 15%. This error bar was not low, but it was

deemed satisfactory for the purpose of the discussion below.

3. Results and discussion

As listed in Table 1, the compounds from the graphite arc-discharge in the atmosphere with varying partial pressure of He/CCl_4 included different carbon species such as graphite, fullerenes (e.g. C_{60} , C_{70} , C_{84} , C_{98}), chlorinated fullerenes (e.g. C_{60}Cl_6 , C_{60}Cl_8), and a series of CCCs (e.g. C_{12}Cl_8 , $\text{C}_{16}\text{Cl}_{10}$, $\text{C}_{18}\text{Cl}_{10}$, $\text{C}_{20}\text{Cl}_{10}$ and their isomers; the isomers are referred as isomer **I** or **II** hereinafter). Fig. 1 shows a typical HPLC-MS chromatogram (recorded under the chromatographic condition **A**) of the toluene-soluble products from graphite arc-discharge at the partial pressure of 40 Torr CCl_4 and 300 Torr He. The structures of some CCCs were determined from their molecular formulas coupled with the characteristic retention times in comparable chromatography of reference compounds identified in our previously allied studies [16–18,21]. Other CCCs have no structural proofs, but their compositions were unambiguously identified by their characteristic isotopic cluster pattern of the molecular ion as shown in the inset to Fig. 1.

Hirsch et al. [13] carried out the graphite arc-discharge experiment with Cl_2 , and identified the main

Table 1
The compositions of the products analyzed under the two chromatographic conditions

Formula (retention time, min) detected under condition A	Formula (retention time, min) detected under condition B
C_6Cl_6 (7.4)	C_6Cl_6 (2.7)
C_8Cl_8 (6.8)	C_{10}Cl_8 (3.0)
C_{10}Cl_8 (18.0)	C_{12}Cl_8 (II) (4.2)
$\text{C}_{11}\text{Cl}_{10}$ (14.3)	C_{14}Cl_8 (3.4)
C_{12}Cl_8 (I) (19.2)	C_{14}Cl_8 (II) (5.0)
C_{12}Cl_8 (II) (40.8)	$\text{C}_{16}\text{Cl}_{10}$ (I) (4.5)
C_{14}Cl_8 (I) (24.7)	$\text{C}_{16}\text{Cl}_{10}$ (II) (6.7)
C_{14}Cl_8 (II) (63.0)	$\text{C}_{18}\text{Cl}_{10}$ (II) (8.0)
$\text{C}_{15}\text{Cl}_8\text{O}$ (28.7)	$\text{C}_{18}\text{Cl}_{10}$ (I) (14.2)
$\text{C}_{16}\text{Cl}_{10}$ (I) (46.0)	$\text{C}_{20}\text{Cl}_{10}$ (I) (4.8)
$\text{C}_{16}\text{Cl}_{10}$ (II) (73.7)	$\text{C}_{20}\text{Cl}_{10}$ (II) (8.2)
$\text{C}_{18}\text{Cl}_{10}$ (II) (110.4)	$\text{C}_{22}\text{Cl}_{10}$ (I) (4.9)
$\text{C}_{18}\text{Cl}_{10}$ (I) (161.7)	$\text{C}_{22}\text{Cl}_{10}$ (II) (8.4)
$\text{C}_{20}\text{Cl}_{10}$ (I) (84.7)	$\text{C}_{28}\text{Cl}_{10}$ (7.6)
$\text{C}_{20}\text{Cl}_{10}$ (II) (180)	C_{32}Cl_8 (10.2)
$\text{C}_{22}\text{Cl}_{10}$ (43.1)	$\text{C}_{50}\text{Cl}_{10}$ (13.6)
$\text{C}_{32}\text{Cl}_{12}$ (43.6)	C_{60} (6.1)
C_{60} (174.8)	C_{60}O (10.6)
C_{60}O (160.0)	C_{60}Cl_8 (14.1)
C_{70} (223.3)	C_{60}Cl_6 (56.6)
	C_{70} (10.4)
	C_{80}O_2 (51.2)
	C_{84} (49.0)
	C_{98} (66.4)
	C_{101} (69.2)

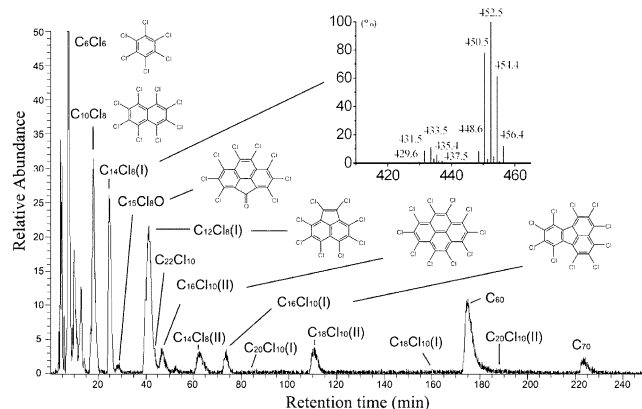


Fig. 1. Typical HPLC-MS total ion current chromatogram (recorded under chromatographic condition A) of the products from the graphite discharge in the presence of CCl_4 (40 Torr) and He (300 Torr). Except the unidentified components, marked peaks are labeled by their molecular formula or/and structures suggested from their isotope distributions in mass spectra (as shown in inset) or the characteristic retention times of reference compounds in comparable chromatography [18].

components of the products as perchlorobenzene (C_6Cl_6 , 60%) and perchloroacenaphthylene (C_{12}Cl_8 , 9%), as well as a small amount of fullerenes (less than 5%) and other CCCs (in total 17%) such as perchloro-coroannulene ($\text{C}_{20}\text{Cl}_{10}$). Alexakis et al. [22–24] designed a PyroGenesis process for fullerene synthesis from C_2Cl_4 based on a DC plasma technology, 2.1% carbon was transferred to fullerenes from C_2Cl_4 under optimal reaction conditions. By means of HPLC- and gas chromatography-mass spectra analyses, the CCCs including C_6Cl_6 , C_{10}Cl_8 , C_{12}Cl_8 , C_{14}Cl_8 and $\text{C}_{16}\text{Cl}_{10}$ were also observed as by-products in their DC plasma process. Although the synthetic methods and reactant sources (chlorine and carbon) employed in Hirsch and Alexakis' experiments were different from the present one, the products of fullerenes and CCCs were approximately similar. This might imply that the three chlorine-involving processes shared a similar route for fullerenes and CCCs growth. Alexakis et al. proposed that reaction temperature is a critical factor for fullerene yield, and the presence of these CCCs might be due to termination of fullerene precursors, which were not given an adequate residence time in the high temperature fullerene formation zone [22–24].

To further investigate the relation between fullerene and the CCCs produced in the chlorine-involving synthetic process, the graphite arc-discharge reaction was performed at the constant CCl_4 partial pressure of 40 Torr with increasing He partial pressures from 0 to 300 Torr. The yields of fullerenes and CCCs from 12 experiments carried out in different He pressure conditions (as shown in Fig. 2a and b) and determined under the chromatographic condition A were clearly dependent on the He/ CCl_4 ratio. The variations of the yields/

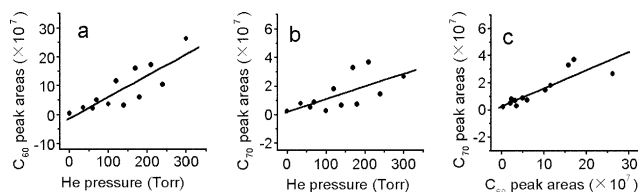


Fig. 2. Fullerenes C_{60} or C_{70} produced under 12 different pressures of He and the YCP of C_{70} vs C_{60} .

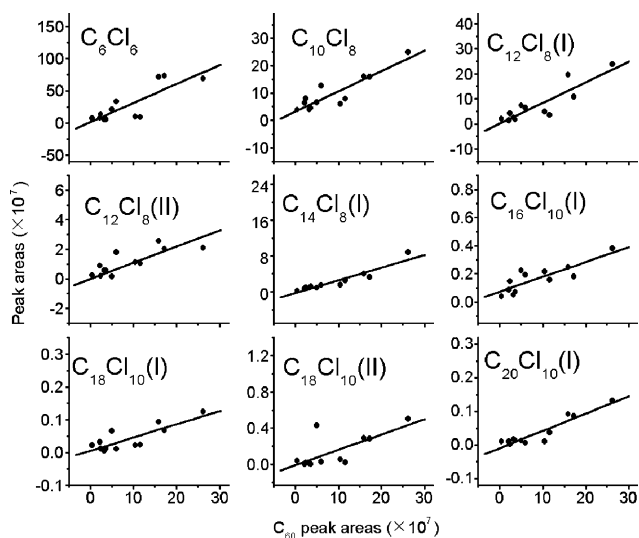


Fig. 3. Linear YCP of CCCs vs C_{60} (Group 1).

peak areas against He pressures are shown in Figs. 2–4. The yields of C_{60} and C_{70} are approximately proportional to the He partial pressure increases (Fig. 2a and b), and C_{70} yields are linearly correlated to the C_{60} yields (Fig. 2c); such plots are hence referred as yield correlation plots (YCP). This is a clear indication that both formations for these two fullerenes (C_{60} and C_{70}) share a common mechanistic pathway. Significantly, the YCP of CCCs vs C_{60} yield at increasing He pressures can be classified in two groups. Group 1 exhibited a linear correlation with positive slopes and consists of smaller CCCs, such as C_6Cl_6 (perchlorobenzene), C_{10}Cl_8 (perchloronaphthalene), C_{12}Cl_8 (perchloroacenaphthylene, isomer I), C_{12}Cl_8 (isomer II), C_{14}Cl_8 (isomer I), $\text{C}_{16}\text{Cl}_{10}$

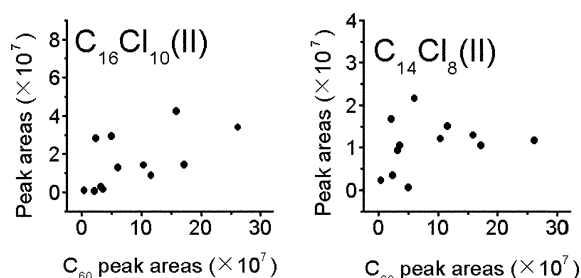


Fig. 4. Random relationship between CCCs and C_{60} (Group 2).

(perchlorofluoranthene, isomer I), $C_{18}Cl_{10}$ (isomer I and II), and $C_{20}Cl_{10}$ (isomer I) as shown in Fig. 3; most of their structures are known as the fragments of fullerenes. Group 2, including $C_{14}Cl_8$ (isomer II) and $C_{16}Cl_{10}$ (perchloropyrene, isomer II), exhibited random scatters of attempted YCP plots as shown in Fig. 4. The displayed result apparently dictates that members of Groups 1 are intimately related to the formation of fullerenes, and those of Group 2 are unrelated side-products. It is assumed that the CCCs in Group 1 are the blind alley from trapping reaction (i.e. end products), and do not participate in the further fullerene formation under the experimental conditions. But their precursors, the energetic reactive species with their attendant structures, known and logically assumed to have pentagon, are the genuine intermediates and excellent sources to evaluate the fullerene formation mechanism. The increasing trend of Group 1 yields suggests more trapping at higher concentration of fullerene precursors when He pressure increasing. Such a process has similar pathway as supposed by Alexakis and co-workers [22–24], but we have made a further observation to distinguish the CCCs in relation with fullerene formation in the chlorine-involving process.

The fullerenes production was reported to be favored under the moderate pressure of He buffer gas ranging from 100 to 400 Torr in the graphite arc-discharge [1,25–27]. We discovered that while the addition of a small partial pressure (e.g. 10 Torr) of CCl_4 into the He medium significantly favored the fullerenes yield, further increase in the CCl_4 pressure from 10 to 100 Torr caused a decrease in the fullerene yield in a non-linear fashion, but on the other hand increased CCCs yield [28]. Accordingly, the YCP of CCCs vs C_{60} was deviated from linear correlation by changing the CCl_4 pressure. The opposing trend of variations can be understood in terms of the trapping of nascent state small carbon clusters which is powerfully reactive owing to the unpaired free electrons in energetic states as discussed previously [16,17,28]. The reactive clusters either couple to grow to fullerenes or get trapped by chlorine sources to form CCCs as the end products. Under the discharge conditions, equilibrium between the carbon clusters and CCCs depends on the concentration/pressure of CCl_4 . When the pressure of CCl_4 was changed, the bonding/dissociation equilibrium shifts [29], subsequently leading to the deviation of YCP correlation.

The large carbon clusters with 10 or 12 free bonds, e.g. $C_{22}Cl_{10}$, $C_{28}Cl_{10}$, $C_{32}Cl_{12}$, and $C_{50}Cl_{10}$ detected in the products (see Table 1), must incorporate varying units of pentagons that cause curvature on the surface of aromatic conjugated networks or form small closed-cage fullerenes from structural demands [30]. Their abundances in the end products, however, were too low to further investigate their relationship with fullerenes formation. Undoubtedly as the analytical process

become more efficient, further evidence can be added leading to better understanding of fullerenes formation.

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