

Synthesis, Separation, and Characterization of Fullerenes and Their Chlorinated Fragments in the Glow Discharge Reaction of Chloroform

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Fullerenes and various chlorinated carbon clusters were synthesized via the glow discharge reaction using chloroform vapor as starting reactant. High-performance liquid chromatography combined with ultraviolet spectrometry and mass spectrometry (HPLC–UV–MS) was developed for separation and characterization of the reaction products, comprising C₆₀ and C₇₀ fullerenes, amorphous carbon, and more than 50 chlorinated carbon clusters, which molecular formulas were determined from their special isotopic patterns. The formation of fullerenes and amorphous carbon in the glow discharge reaction of chloroform was found to involve different systems of chlorinated carbon cluster intermediates. The correlation provides insight into the formation of fullerenes and the other carbon clusters.

Introduction

Fullerenes can be accessed via thermal reaction of appropriate carbon sources under various conditions, for instance, arc-discharge of graphite rods,¹ incomplete combustion of benzene or hydrocarbons,² pyrolysis of naphthalene,³ and dissociation of hydrocarbons in thermal plasma.^{4–7} Efforts to develop traditional organic methods to synthesize fullerenes have not achieved success yet, but various bowl-shaped hydrocarbons have been produced by pyrolytic or nonpyrolytic routes.^{8–22} In our prior investigation,²³ fullerenes C₆₀ and C₇₀ were produced from chloroform in a glow discharge reaction, known as a typical low-temperature plasma.²⁴ It was found in the experiment that the fullerenes were accompanied by various fully chlorinated fullerene fragments such as perchloroacene (C₁₂Cl₈) and perchlorofluoranthene (C₁₆Cl₁₀), which carbon frameworks composed of six- and five-membered rings can be identified as part of the surface of fullerenes. Herein the synthetic reaction and analysis of the products from the glow plasma reaction of chloroform are reported in detail. High-performance liquid chromatography coupled with both ultraviolet spectrometry and mass spectrometry (HPLC–UV–MS) was developed for separation and characterization of the fullerene products as well as a series of chlorinated carbon clusters. Special attention was paid to the correlation between the fullerenes and the chlorinated carbon clusters formed in the same reaction. The experimental observation reported herein is not only synthetically useful but may also provide some important insight into fullerene formation.

Experimental Section

Chemicals. Solvents used in the experiment were commercially available. Methanol was HPLC grade, and other solvents were analytical grade. All HPLC solvents were further distilled and degassed by vacuum filtration over a 0.45 μm membrane filter prior to use.

Soot Production. The experimental setup is illustrated in Figure 1. Chloroform was evaporated from a flask into reaction

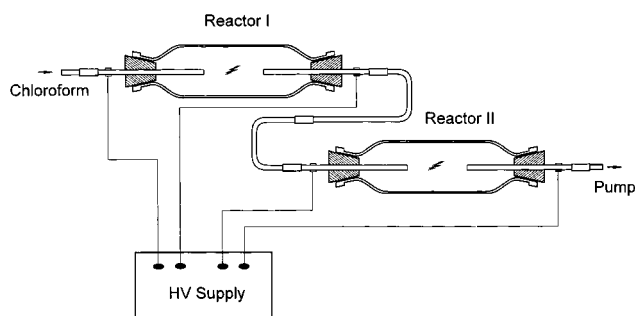


Figure 1. Scheme of the glow discharge reactors.

chambers, two glass tubes with diameter of ca. 40 mm and length of ca. 250 mm. Two pairs of copper pipes, acting as both electrodes and gas passageway, were mounted to two ends of each tube. When the vacuum pressure of the tubes was pumped to less than 0.004 MPa and an alternate voltage of above 10 kV with 25 kHz frequency was applied to the electrodes, a stable glow discharge would emerge at the gap between the two electrodes. The glow plasma could be maintained by adjusting the distance between the electrodes. In the synthetic experiment, the two reactors, labeled in the figure as reactor I and reactor II, were connected in series. After reaction for several hours, soot produced from the discharge reaction was deposited on the wall of each reactor and then collected separately from the two reactors, followed by separation and identification using HPLC–UV–MS.

Effects of various experimental parameters on the glow plasma were investigated in the experiment. It was found in the preliminary experiment that glow plasma was very sensitive to the reaction conditions, such as vacuum of the reactor, feed rate of the chloroform vapor, and electrical voltage and frequency. Relatively high vacuum in the reactor was necessary for the plasma reaction. When the pressure was greater than 0.01 MPa, the plasma could not be maintained. Raising feed rate of the chloroform vapor would improve the reaction efficiency but with the cost of disturbing the plasma. In fact, the plasma would die out when feed rate of the reactant was higher than 0.6 mL/min. Yield of the soot was also found to

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depend on the electrical field applied in the reaction, especially its frequency. Increase of the frequency generally resulted in the raise of the soot yield. The optimum conditions used for the experiment were as follows: vacuum, 0.004 Mpa; feed rate of the chloroform vapor, 0.3 mL/min; electrical frequency, 25 kHz. Under these conditions, the soot could be produced in a yield of 3 g/h.

Sample Preparation. Approximately 500 mg of the soot from the glow discharge reaction of chloroform and 5 mL of toluene were placed in a glass container with a cap. This suspension was extracted using ultrasonic bath at room temperature for 1.5 h, allowed to settle for about 2 h, and then filtered using a 0.45 μm pore membrane filter. The solution was loaded into the instruments for HPLC–UV–MS analysis.

HPLC–UV–MS Analysis. The instruments used for HPLC–UV–MS analysis were a TSP model P200 HPLC equipped with a TSP UV 3000 spectrophotometer and a Finnigan LCQ model mass spectrometer with APCI interface.

The TSP UV 3000 instrument consisted of rapid scan UV spectrophotometric detection. This technique, involving the continuous acquisition of UV spectra, is highly sensitive to characterize fullerenes and the polycyclic carbon clusters, as peaks eluted from the HPLC column. Absorption spectrum was recorded over 210–400 nm wavelength range. Scan resolution and data collection rates of the spectrometer were fixed at 5 nm and 6.7 Hz, respectively.

The Finnigan LCQ mass spectrometer consisted of an atmospheric pressure chemical ionization (APCI) source and an ion-trap mass analyzer. The APCI vaporization temperature was 400 °C. Mass spectra were recorded within the range of m/z 200–2000 in negative ion mode. Flow rates of sheath gas and auxiliary gas were 70 and 20 mL/min, respectively. Capillary temperature and voltage were 200 °C and –28 V, respectively.

Combination of the instruments was achieved by simply connecting the outlet of the HPLC detector to the inlet of the APCI interface of the mass spectrometer. The HPLC–UV data and the HPLC–MS data were collected by different computer systems.

The HPLC column selected for analysis was a SUPELCOSIL LC-18 column with 4.6 mm i.d. and 250 mm in length, packed with 5 μm octadecylsilyl-bonded silica having a 300 Å pore size. Nonaqueous reversed-phase HPLC was selected considering the low volatility and high lipophilicity of fullerenes and chlorinated carbon clusters. To record UV spectra of the reaction products, the mobile phase needs to be transparent or have low absorption in the wavelength region of 210–400 nm. Thus, only a few solvents, such as methanol, ethanol, acetonitrile, tetrahydrofuran, hexane, and cyclohexane, could satisfy the requirements. Among the selections, low-polar solvent was good for the solution of the products but lack of retention, while some products from glow plasma of chloroform could not elute out the octadecylsilyl-bonded silica column thoroughly when polar solvents were applied. Hence, a binary or multiple mobile phase mixed by polar and low-polar solvents in a certain ratio might be a better choice. After testing of various combinations of the mixtures, it was found that mixed solvents of cyclohexane/ethanol/methanol could be used as mobile phase for the separation in a gradient elution mode. The elution procedure of the mobile phase consisted of a linear increase in cyclohexane concentration from 0 to 5% in 40 min and from 5% to 35% in the next 180 min and a linear decrease in methanol from 85 to 80% in 40 min and from 80% to 54% in the next 180 min. Ethanol was premixed with methanol in a 2:11 ratio, which was not varied

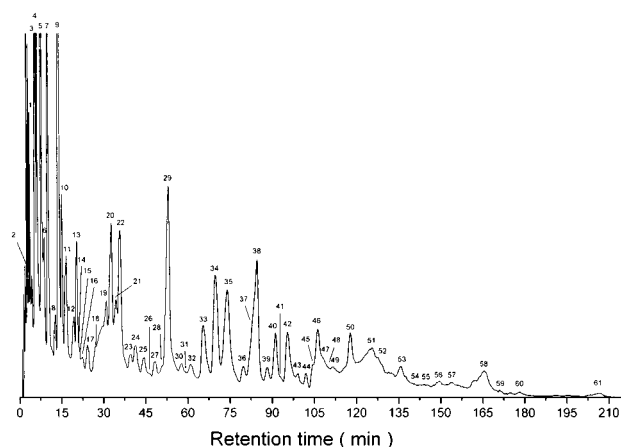


Figure 2. Typical HPLC–UV chromatogram of products collected in reactor I and recorded at 300 nm wavelength. Peaks are labeled by numbers, and their molecular formula are suggested from their isotope distributions in mass spectra as the following: 1, C_5HCl_5 ; 2, $\text{C}_{58}\text{Cl}_{12}$; 3, C_8Cl_8 ; 4, C_6Cl_6 ; 5, $\text{C}_8\text{H}_3\text{Cl}_5$; 6, $\text{C}_{14}\text{Cl}_{14}$; 7, C_8Cl_6 ; 8, $\text{C}_{22}\text{Cl}_{14}$; 9, C_{10}Cl_8 ; 10, C_{12}Cl_8 ; 11, $\text{C}_{14}\text{Cl}_{14}$; 12, $\text{C}_{18}\text{Cl}_{14}$; 13, C_{14}Cl_8 ; 14, $\text{C}_{28}\text{Cl}_{16}$; 15, $\text{C}_{20}\text{Cl}_{14}$; 16, $\text{C}_{12}\text{Cl}_{12}$; 17, $\text{C}_{24}\text{Cl}_{14}$; 18, $\text{C}_{14}\text{Cl}_{10}$; 19, $\text{C}_{14}\text{Cl}_{12}$; 20, $\text{C}_{12}\text{Cl}_{18}$; 21, $\text{C}_{30}\text{Cl}_{14}$; 22, $\text{C}_{20}\text{Cl}_{14}$; 23, $\text{C}_{51}\text{Cl}_{12}$; 24, $\text{C}_{22}\text{Cl}_{16}$; 25, $\text{C}_{16}\text{Cl}_{10}$; 26, $\text{C}_{18}\text{Cl}_{14}$; 27, $\text{C}_{12}\text{Cl}_{14}$; 28, $\text{C}_{14}\text{Cl}_{18}$; 29, $\text{C}_{30}\text{Cl}_{14}$; 30, $\text{C}_{22}\text{Cl}_{12}$; 31, $\text{C}_{26}\text{Cl}_{14}$; 32, $\text{C}_{16}\text{Cl}_{10}$; 33, $\text{C}_{26}\text{Cl}_{12}$; 34, $\text{C}_{22}\text{Cl}_{14}$; 35, $\text{C}_{20}\text{Cl}_{14}$; 36, $\text{C}_{50}\text{Cl}_{12}$; 37, $\text{C}_{20}\text{Cl}_{10}$; 38, $\text{C}_{20}\text{Cl}_{14}$; 39, $\text{C}_{18}\text{Cl}_{10}$; 40, $\text{C}_{28}\text{Cl}_{10}$; 41, $\text{C}_{60}(\text{IV})$; 42, $\text{C}_{32}\text{Cl}_{12}$; 43, $\text{C}_{26}\text{Cl}_{10}$; 44, $\text{C}_{30}\text{Cl}_{10}$; 45, $\text{C}_{50}\text{Cl}_{10}$; 46, $\text{C}_{36}\text{Cl}_{10}$; 47, $\text{C}_{26}\text{Cl}_{10}$; 48, $\text{C}_{60}(\text{III})$; 49, $\text{C}_{24}\text{Cl}_{12}$; 50, $\text{C}_{22}\text{Cl}_{12}$; 51, C_{60}Cl_8 ; 52, $\text{C}_{24}\text{Cl}_{12}$; 53, $\text{C}_{18}\text{Cl}_{10}$; 54, $\text{C}_{34}\text{Cl}_{12}$; 55, $\text{C}_{60}(\text{II})$; 56, $\text{C}_{26}\text{Cl}_{10}$; 57, $\text{C}_{28}\text{Cl}_{10}$; 58, $\text{C}_{60}(\text{I})$; 59, $\text{C}_{32}\text{Cl}_{10}$; 60, $\text{C}_{28}\text{Cl}_{10}$; 61, C_{70} .

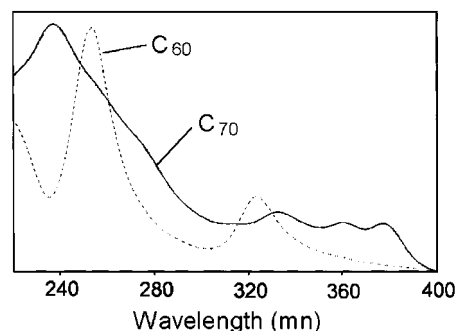


Figure 3. UV adsorption spectra of C_{60} and C_{70} fullerenes.

during the elution process. Flow rate of the mobile phase was set at 1.0 mL/min, and sample injection was quantified with a 20 μL loop.

Results and Discussion

Production and Identification of C_{60} and C_{70} Fullerenes.

The toluene extract of the products from glow discharge reaction of chloroform was analyzed by HPLC–UV–MS under the optimum conditions, and a typical chromatogram of products collected from reactor I is shown in Figure 2. It could be found in the chromatogram that the products from the reaction were quite complicated, but most of them, C_{60} and C_{70} fullerenes as well as various chlorinated carbon clusters, can be separated under the HPLC analysis condition mentioned above. As shown in Figure 3, the UV spectra obtained at retention times of 167 and 209 min were virtually identical to those of standard C_{60} and C_{70} .^{1,25} Identities of C_{60} and C_{70} fullerenes suggested by the UV spectra were also confirmed by their retention time after comparing with those of the standard ones and by the mass distributions of their molecular ions observed in corresponding mass spectra. The analysis result showed that fullerenes could be synthesized in the glow discharge reaction of chloroform under a relatively low-temperature plasma condition.

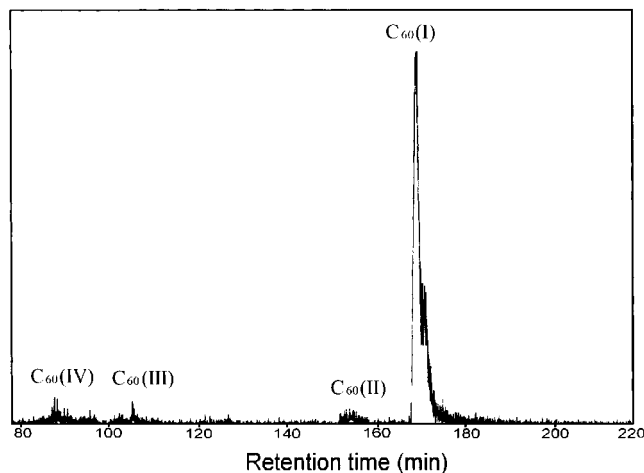


Figure 4. Selected HPLC-MS ion chromatogram of possible C_{60} isomers in the range of m/z 720–722.

In comparison to what has been achieved by arc discharge methods,¹ fullerene yield by this synthetic reaction was relatively low. However, the synthesis reported herein was a preliminary study and various parameters remain to be further optimized for fullerene production. In addition, the synthetic reaction could be operated continuously so that the device could be easily scaled up. Especially, the reaction was performed in a low-temperature plasma that differs from other synthetic methods,^{1–7} so the synthetic reaction merits special attention in fullerene science.

As shown in Figure 4, the selected-ion chromatogram of the products collected in reactor I in the ranges of m/z 720–722, besides the dominant peaks corresponding to buckminsterfullerene, three other 720 amu ions were also observed at the retention times of 92, 108, and 155 min. These ions are suggested as novel C_{60} isomers according to their isotope distributions in the mass spectra. These mass spectra evidences, however, might also result from C_{60} adducts (e.g. with chlorine), on the basis of the hypothesis that such adducts formed in the glow plasma reaction but dissociated to be C_{60}^- during the ionization process. In fact, this evidence had also been observed in HPLC-MS analysis of products from benzene-oxygen flames^{26,27} and microwave plasma reaction of chloroform.²⁸ Unfortunately, the HPLC-MS characterization is insufficient to determine their structures. Our effort focusing on preparative separation and structural characterization of these newly observed carbon clusters with 720 amu is in process.

Production and Identification of Chlorinated Carbon Clusters. Fullerene formation in the glow discharge reaction of chloroform is a growth process from small clusters, analogous to the growth of polycyclic aromatic hydrocarbons.^{29,30} In fact, in addition to fullerenes and amorphous carbon, other carbon clusters with intermediate sizes were also produced in the reaction, but most of them were chlorine-substituted to eliminate the dangling bonds. Luckily, mass spectrometry is effective in analyzing the compositions of these chlorinated products because the two isotopes of chlorine have their special abundance distribution: $^{35}\text{Cl}:^{37}\text{Cl} = 75.77:24.23$. Thus, isotopic distributions of the compounds containing different numbers of chlorine atoms can be calculated. By comparison of the simulated distribution with the recorded mass spectrum, the number of chlorine atoms and the number of carbon atoms in each chlorinated carbon cluster can be readily determined, and thus its molecular formula characterized. As examples, Figure 5 shows typical isotope distributions of selected chlorinated carbon clusters, $C_{58}\text{Cl}_{12}$, $C_{12}\text{Cl}_8$, $C_{22}\text{Cl}_{14}$, and $C_{18}\text{Cl}_{10}$, which were

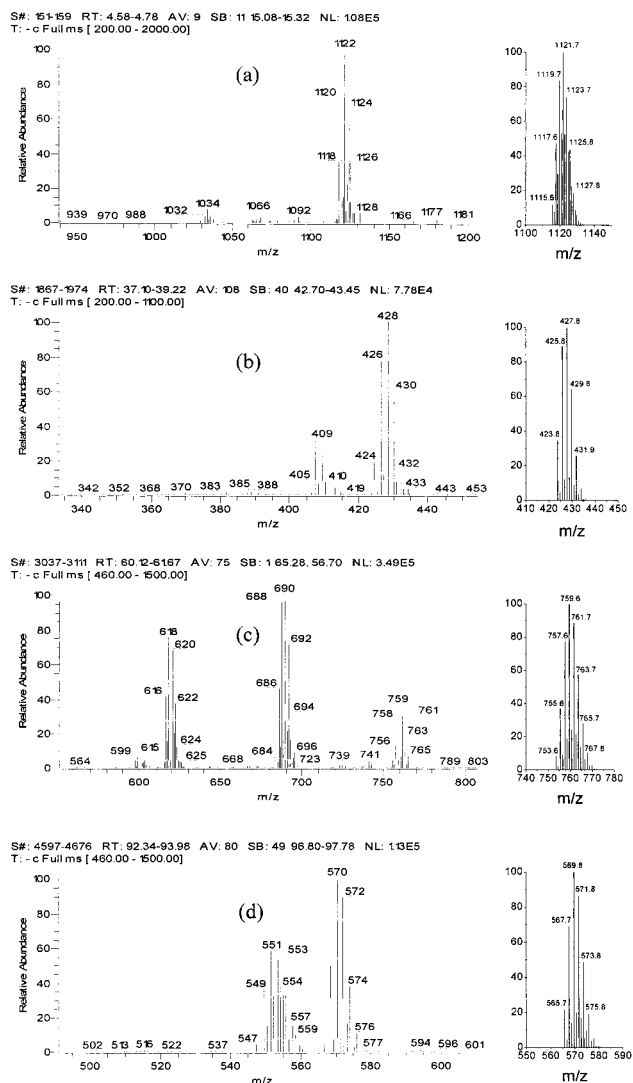


Figure 5. Isotope distributions of selected chlorinated carbon clusters recorded in mass spectra: (a) $C_{58}\text{Cl}_{12}$ (no. 2); (b) $C_{12}\text{Cl}_8$ (no. 20); (c) $C_{22}\text{Cl}_{14}$ (no. 34); (d) $C_{18}\text{Cl}_{10}$ (no. 39). Simulated distributions of their molecular ions peaks are inserted at the right of the figures.

recorded in the experiment. Simulated distributions of their molecular ions peaks are included in the figures for better identification. In addition to the molecular ions peaks, ions peaks with weights 19 less than their molecular weights were also observed in the figures, and they might result from the clusters losing a chloride atom and capturing an oxygen anion in the APCI source.³¹

Correlation between Fullerenes and Chlorinated Carbon Clusters. All the products in the reaction, fullerenes, amorphous carbon, and chlorinated carbon clusters, were created under the same reaction condition and from the same starting species, chloroform, a simple molecule composed of a single carbon atom. It was thus reasonable to conjecture that the small carbon clusters, which were chlorinated in the reaction, might be the precursors of larger carbon species such as fullerenes and amorphous carbons. Most of the small carbon clusters, however, could not grow up in the reaction. As shown in Figure 2, the relative abundance of the products is generally reduced with an increase of their carbon number. In fact, the small carbon clusters initially produced in the plasma were generally very reactive. To survive the plasma, their dangling bonds need to be saturated by radicals such as chlorine atoms which are also produced in great amount in the glow plasma. The growth of

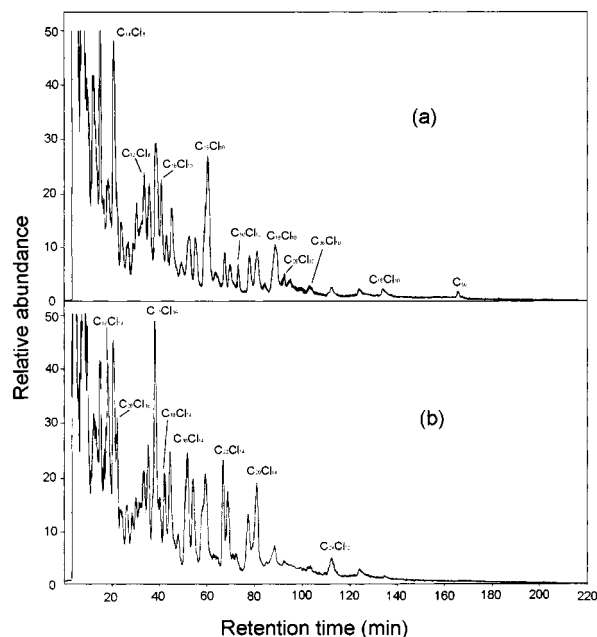


Figure 6. HPLC-MS chromatograms of the reaction products: (a) products A collected in reactor I; (b) products B collected in reactor II.

most small carbon clusters is thus stopped before they reach larger aggregates, fullerenes, or amorphous carbons, which have no dangling bonds at all.

It would be more interesting to distinguish the precursors leading to the fullerenes and other carbon species. In the experiment, two reactors, labeled as reactors I and II in Figure 1, were connected in series. The products from reactors I and II were collected separately and were distinguished as products A and B, respectively. As shown in Figure 6a,b, the HPLC-MS chromatograms of products A and B, respectively, the species forming in the two reactors were similar, but their relative yields were significantly different. The fullerene yield in products B was markedly less than that in products A. Further quantitative analysis indicated that C_{60} yield in products A was 0.5% and that in products B was less than 0.05%. On the other hand, in reactor II, production of amorphous carbon, which was identified by X-ray diffraction analysis, was much higher than that in reactor I. Similarly, chlorinated carbon clusters with different compositions were also produced in different yields in the two reactors. Generally, as shown in Figure 6, the clusters produced in reactor I tend to consist of less chlorine atoms than those produced in reactor II. We thus supposed that there might be two systems of small carbon clusters produced in the experiment, and they displayed different relative abundances in the final products grown in the two reactors.

Different distributions of the chlorinated carbon clusters produced in the different reactors might be attributed to their different structures. As shown in Figure 6a, most of chlorinated carbon clusters with higher abundance produced in reactor I was composed of 8–12 Cl atoms and even numbers of carbon atoms. Among them, structures of small clusters, such as $C_{12}Cl_8$, $C_{16}Cl_{10}$, and $C_{20}Cl_{10}$, have been characterized before.^{23,32} Their carbon frameworks, comprising six- and five-membered rings, could be identified as part of the surface of buckminsterfullerene. The larger clusters in the series which also exhibited higher abundance in products A, such as $C_{18}Cl_{10}$, $C_{28}Cl_{10}$, $C_{36}Cl_{10}$, and $C_{58}Cl_{12}$, might be chlorinated fullerene fragments as well, according to their compositions and the structures of their hydrocarbon analogues,^{12–22} though charac-

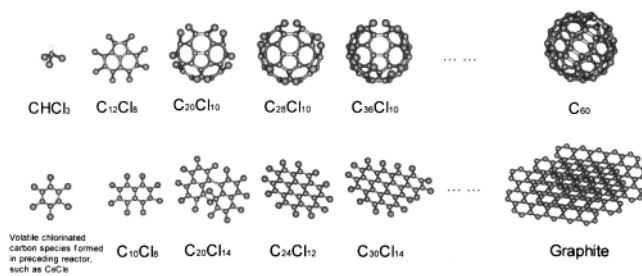


Figure 7. Growth scheme of fullerene and graphite. C_{60} , graphite, and chlorinated carbon clusters shown in the figure were the products of the glow discharge reaction. Molecular formulas labeled in the figure were characterized by their isotope distributions in corresponding mass spectra. Structures of the small perchlorinated carbon clusters, such as $C_{10}Cl_8$, $C_{12}Cl_8$, $C_{16}Cl_{10}$, and $C_{20}Cl_{10}$, had been characterized before, and structures of the large clusters, such as $C_{20}Cl_{14}$, $C_{28}Cl_{10}$, $C_{30}Cl_{14}$, and $C_{36}Cl_{10}$, were suggested according to their special compositions, while their structural identification is still in process.

terization of their structures is still in progress. In these structures, pentagons are incorporated into their polycyclic networks and cause curvature so that C-Cl bonds of these clusters are minimized and generally do not increase with the number of carbon atoms. Since all these chlorinated clusters and the fullerenes grew from chloroform in a same reaction, their formation may follow the same reaction mechanism: adding C_2 or other small carbon particles to the developing graphite sheet. The dangling bonds on the rim of the carbon framework were saturated by chlorine atoms, and the closed fullerenes, once formed, have no open edges and, therefore, generally do not grow any further. The growth mechanism is just the one described by the “pentagon road” scheme,³³ one of the schemes that have been proposed for fullerenes formation. Hence, this system of chlorinated carbon clusters can be regarded as fullerene precursors or chlorinated intermediates in fullerenes growth following the scheme of “pentagon road”.

Besides the carbon clusters derived with 8–12 chlorines, the clusters comprising more chlorine atoms were also produced during the reaction in a great variety and were found to be more abundant in products B. In contrast to the clusters described above, the number of chlorine atoms in this system of clusters increases with their number of carbons. The compositions suggested that frameworks of this system of polycyclic carbon clusters were planar and very likely the fragments of the graphite. Higher yield of the observed amorphous carbons in products B, which were in fact the microcrystals of graphite, supports this hypothesis. A scheme of growth pathways of the two elementary carbon species is illustrated in Figure 7, but it should be noted that many structures of the chlorinated carbon clusters pictured here were speculated on the basis of their compositions.

In the glow discharge experiment, the reactions in the two reactors were carried out under the same vacuum and sharing the same electrical power source but were fed different starting reactants. In reactor I, the reactant was chloroform vapor, while the reactants in reactor II were composed of variety of volatile chlorinated carbon species formed in the preceding reactor, such as C_4 or C_6 .³⁴ The experimental evidence suggested the possibility of designing the proper precursors so as to improve fullerene yield in the synthetic reaction. Our effort on this purpose is currently in process.

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