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LETTERS

Formation of Buckminsterfullerene and Its Perchlorinated Fragments by Laser Ablation of Perchloroacenaphthylene

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Perchloroacenaphthylene($C_{12}Cl_8$), a perchlorinated polycyclic hydrocarbon composed of two hexagons and a pentagon, was ablated by a pulsed laser beam in a vacuum. The products created from the laser ablation were characterized by high-performance liquid chromatography coupled with atmospheric pressure chemical ionization mass spectrometry and rapid-scan ultraviolet spectrophotometric detection. Buckminsterfullerene C_{60} and various perchlorinated carbon clusters have been observed among the products. The observation is helpful for understanding the formation mechanisms of fullerenes and suggests that the Pentagon Road scheme is feasible with the involvement of chlorines.

I. Introduction

Despite the great efforts in recent years,[1,2] growth mechanisms of fullerenes have not yet been well understood. As early as fullerenes were produced and detected in mass spectrometry, various mechanisms have been proposed for the fullerene formation process.[3−6] Among them, the Pentagon Road mechanism was postulated at first.[6] According to the mechanism, fullerenes grow by adding C_2 and other small carbon particles to the reactive edges of the developing graphite cups. Subsequently, many efforts toward understanding fullerenes growth have been taken by synthesis chemists,[7,8] and various curved polycyclic aromatic hydrocarbons were obtained, such as $C_{20}H_{10}$,[9−14] $C_{30}H_{12}$,[14−17] and $C_{36}H_{12}$,[18−21] which were predicted in the Pentagon Road scenario. The scheme, however, is lacking experimental evidence to support the conversion of C_{60} from curved graphite intermediates at the key stage of C_{60} formation.

Shortly before the macroscopic synthesis of buckminsterfullerene (C_{60}), growing experimental evidence indicates that fullerene formation can occur through ring coalescence and annealing.[22] Following laser desorption of cyclic molecules, such as $C_{30}(CO)_{10}$, McElvany et al. observed C_{60}^+ with significant signal intensity in recorded mass spectra.[23] A ring coalescence and annealing mechanism, based on the experiments, appears sufficient to account for most of the carbon clusters' growth.[3] Much of the observed data from mass spectrometry and the

TABLE 1: Typical Conditions for HPLC-MS−UV Analysis

HPLC	UV	APCI-MS
instrument	instrument	instrument
TSP P200 HPLC system	TSP UV3000	Finnigan LCQ
stationary phase	wavelength scan range	vaporization temp
SUPELCOSIL LC-18	220−400 nm	400 °C
5 μm, 25 × 4.6 mm ID	software	sheath gas
mobile phase	PC 1000	N_2 70 mL/min
methanol/ethanol/cyclohexane		auxillary gas
gradient (in 240 min)		N_2 20 mL/min
methanol from 83% to 54%		capillary temp
ethanol from 17% to 11%		200 °C
cyclohexane from 0 to 35%		capillary voltage
flow rate		−28 V
1.0 mL/min		scan range
operation temperature		200−2000 *m/z*
room temp		

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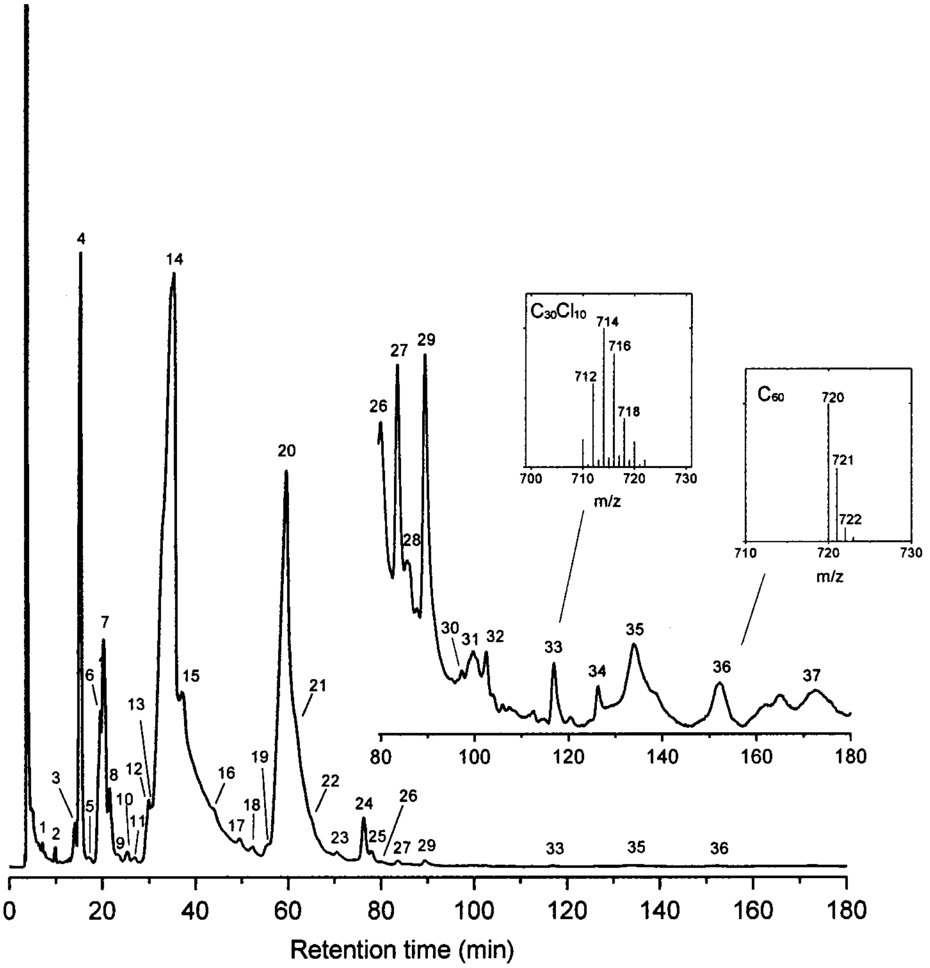

1	C_6Cl_6	2	$C_{12}Cl_{10}$	3	$C_{24}Cl_{12}$	4	$C_{13}Cl_6$
5	$C_{24}Cl_{12}$	6	$C_{20}Cl_{10}$	7	$C_{22}Cl_{10}$	8	$C_{22}Cl_{10}$
9	$C_{10}Cl_{12}$	10	$C_{14}Cl_{10}$	11	$C_{24}Cl_{10}$	12	$C_{28}Cl_{14}$
13	$C_{30}Cl_8$	14	$C_{12}Cl_8$	15	$C_{16}Cl_{10}$	16	$C_{12}Cl_{14}$
17	$C_{30}Cl_{14}$	18	$C_{44}Cl_{12}$	19	$C_{28}Cl_{12}$	20	$C_{16}Cl_{10}$
21	$C_{30}Cl_{14}$	22	$C_{28}Cl_{12}$	23	$C_{32}Cl_{14}$	24	$C_{30}Cl_{12}$
25	$C_{30}Cl_{12}$	26	$C_{36}Cl_{16}$	27	$C_{42}Cl_{10}$	28	$C_{60}Cl_8$
29	$C_{28}Cl_{10}$	30	$C_{33}Cl_{14}$	31	$C_{34}Cl_{14}$	32	$C_{34}Cl_8$
33	$C_{30}Cl_{10}$	34	$C_{20}Cl_{10}$	35	$C_{18}Cl_{10}$	36	C_{60}
37	$C_{32}Cl_{10}$						

Figure 1. HPLC chromatogram of the products recorded at 260 nm wavelength. Peaks are labeled by numbers and their molecular formula as suggested from their mass spectra are shown.

formation experiments of C_{60} from cycloalkynes support this scheme.[2,24,25]

Similar to the experiments of McElvany et al.,[23] which provided important experimental evidence to support the ring coalescence and annealing scheme,[3] we prepared perchloroacenaphthylene ($C_{12}Cl_8$) as precursor to fullerene formation. This precursor has a carbon frame of fullerene fragment predicted in Pentagon Road. In addition, high-performance liquid chromatography (HPLC), coupled with atmospheric pressure chemical ionization mass spectrometry (APCI-MS) and rapid-scan ultraviolet (RS−UV) spectrophotometry (HPLC-MS−UV), was applied for the separation and identification of final products, rather than only MS detection used in the prior experiment.[23] As part of our ongoing effort to synthesis fullerenes and their perchlorinated fragments from multichlorinate methane compound,[26−29] it would be interesting to explore of one of the perchlorinated fragment of fullerene reacting to fullerenes by laser ablation. The experimental result would be informative to reveal the mechanistic puzzle to physical and organic chemists.

II. Experimental Section

We used 1 g of $C_{12}Cl_8$ for the target sample of laser ablation. The compound was synthesized from liquid discharge reaction of chloroform and purified by column chromatography and recrystallization.[29] To analyze the purity of the target sample, we performed HPLC experiment of $C_{12}Cl_8$ under the conditions used in prior paper.[27] The quantitative analysis indicated that its purity was 99.9%.

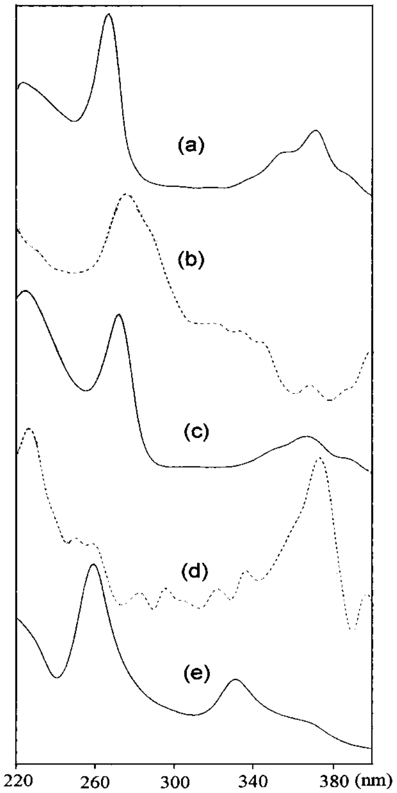

Figure 2. UV spectra of selected products. (a) $C_{12}Cl_8$ (**14**), (b) $C_{18}Cl_{10}$ (**35**), (c) $C_{20}Cl_{10}$ (**6**), (d) $C_{32}Cl_{10}$ (**37**), (e) C_{60} (**36**).

The device used in the laser ablation experiment is a sealed glass tube evacuated to 10^{-3} Torr. To restrict the sample under the laser ablation, the sample was covered with a copper mesh. The focused ablation laser beam penetrates through a small hole at the center of the mesh. The ablation laser operated at 10 Hz is the second harmonic output of a Q-switched Nd:YAG laser, with 15 ns pulse width and 30 mJ output energy. The laser power density on the sample is about 5×10^7 W/cm^2.

After 10 h of ablation, the products from the laser ablation was collected and dissolved in toluene under an ultrasonic bath. After filtration, the resulting reddish brown solution containing dissolved products was separated and analyzed by HPLC with RS−UV spectrophotometric detection. This technique, involving the continuous acquisition of UV spectra, is highly sensitive to characterize fullerenes and polycyclic carbon clusters, as peaks elute from the HPLC column. The products from the UV detector were further analyzed by a mass spectrometer, which is coupled with HPLC by an atmospheric pressure chemical ionization (APCI) source. Typical parameters and conditions of the HPLC−UV-MS analysis are listed in Table 1.

III. Results and Discussion

Figure 1 displays chromatogram of the final products at 260 nm. As shown in the chromatogram, products from the laser ablation are quite complicated, but most of them can be separated by HPLC. Characterized products, including various chlorinated carbon clusters and C_{60}, are labeled in this figure, and their molecular formula suggested from their mass spectra, are listed in the caption.

The experiment shows that C_{60}, identified by comparing its MS/UV spectrum and eluting time in HPLC analysis with that of standard buckminsterfullerene can be created from $C_{12}Cl_8$, but with low abundance among the products of laser ablation. As five-membered ring is essential for the formation of fullerenes as predicted by the Pentagon Road scheme, $C_{12}Cl_8$, which is composed of two hexagons and a pentagon, can be considered as the perchlorinated intermediates in fullerene formation. Hence, it is likely the intermediates, predicted by Pentagon Road scheme, may be involved in the formation of fullerene. Further insights can be deduced by detailed examination of the relative abundance of the products in the recorded HPLC chromatogram (Figure 1). Few compounds smaller than $C_{12}Cl_8$ were also found in the products. Relative abundance of the products generally reduces with increase of their number of carbons. Moreover, C_{60} is less abundant than the other products. Therefore, it is most likely that C_{60} grows directly from $C_{12}Cl_8$, not merely from small carbon species (C_1, C_2, C_3), and growth of many large perchlorinated carbon clusters stopped before they reached to the cage structure of fullerenes. Formation probability of different products thus decreases with increase

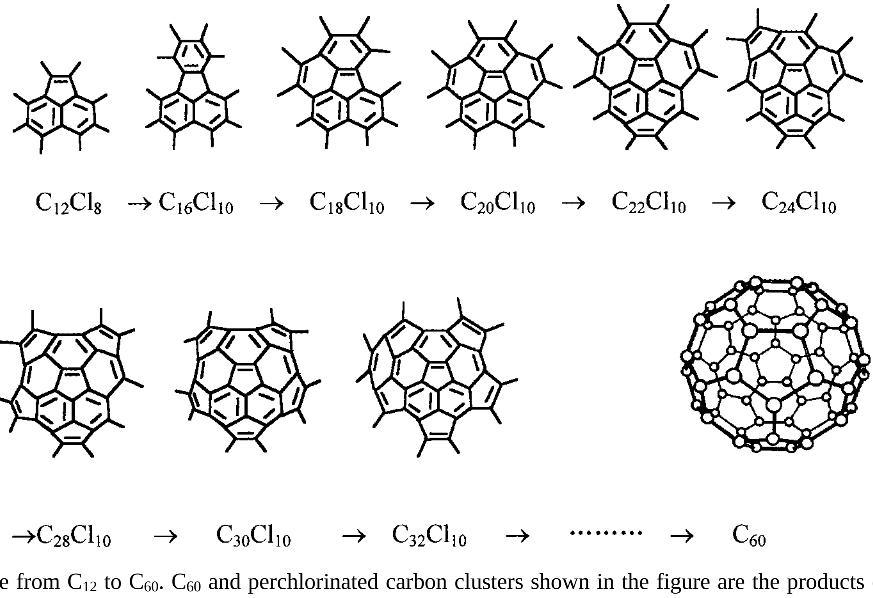

Figure 3. Growth scheme from C_{12} to C_{60}. C_{60} and perchlorinated carbon clusters shown in the figure are the products of the laser ablation. The molecular formula labeled on the figure were determined by mass spectrometry. Structures of the small perchlorinated carbon clusters, such as $C_{16}Cl_{10}$ and $C_{20}Cl_{10}$, have been characterized before,[28,29] and structures of the other chlorinated carbon clusters, such as $C_{18}Cl_{10}$, $C_{22}Cl_{10}$, $C_{24}Cl_{10}$, $C_{28}Cl_{10}$, $C_{30}Cl_{10}$ and $C_{32}Cl_{10}$, are suggested according to their special compositions.

of the cluster size. The proposed formation process may account for the relatively low yields of both C_{60} and larger perchlorinated carbon clusters among the products of the laser ablation reaction.

Chemical molecular formula of the other products was characterized by their mass and isotopic pattern of molecular ion peaks in the recorded mass spectra. As an example, a typical mass spectrum of $C_{30}Cl_{10}$ is inserted in Figure 1. UV spectra of selected products are shown in Figure 2. As shown in the data, most of the products from Laser Ablation are perchlorinated carbon clusters. Among them, structures of the small compounds, such as C_6Cl_6, $C_{12}Cl_8$, $C_{16}Cl_{10}$, and $C_{20}Cl_{10}$, have been characterized before,[28,29] so they would be identified by comparing their HPLC−UV spectra with the standard ones. The carbon frameworks of the molecules, composing of six- and five-membered rings, can be identified as part of the surface of buckminsterfullerene. Most of the larger perchlorinated products from laser ablation of $C_{12}Cl_8$, such as $C_{22}Cl_{10}$, $C_{24}Cl_{10}$, $C_{28}Cl_{10}$, $C_{30}Cl_{10}$, and $C_{32}Cl_{10}$, are composed of 10 Cl atoms and even number of carbon atoms according to the mass spectrometric characterization. With regards to the limited chlorinated derivatives from polycyclic aromatic hydrocarbons (PAHs), their carbon frames are most likely fused polycyclic, and tend to curve with increasing number of carbon atoms. Moreover, typical polycyclic aromatic absorbency at 210−230, 250−270 and 330−380 nm were observed in their UV spectrum (Figure 2). Therefore, they should be fused polycyclic compounds and might also be the perchlorinated fragments of fullerenes (Figure 3), though characterization of their structures is still in progress. In addition, since all these products, including C_{60} and perchlorinated carbon clusters, were created from $C_{12}Cl_8$, it is reasonable to conjecture that formation of the carbon frames of all these products 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 the chlorine atoms, and the closed fullerenes, once formed, have no open edges and, therefore, generally do not grow any further. As indicated in Figure 3, The growth mechanism is just the one described by Pentagon Road scheme.[6]

Up to now, no literature describes the experimental evidence or actual isolation of products from laser ablation of acenaphthylene ($C_{12}H_8$), parent PAHs of $C_{12}Cl_8$. But Vögtle et al.[8] detected traces of C_{60} among the pyrolysis products of various hydrocarbons, and revealed that five-membered rings, from start material or formed during pyrolysis, played a critical role for the growth of fullerene. The occurrence of fullerenes fragments, such as bowl-shaped corannulene($C_{20}H_{10}$), was not mentioned by the author. In this experiment, however, occurrence of the chlorinated fragments of fullerenes does not necessarily contradict the prior experimental evidence: few small carbon clusters or fullerene fragments were obtained in the arc discharge reactions for fullerene synthesis, in which graphite was evaporated in an inert atmosphere.[30] In fact, some larger chlorinated carbon clusters were also found in our ongoing investigation for fullerene synthesis through plasma reaction of chloroform.[26,28,29] These experiments indicate that the stability of fullerene intermediates can be enhanced by involving the chlorine atoms. In the course of fullerene growth, dangling bonds on the rim of carbon framework were saturated by chlorine atom, and the intermediates turn to be stable because of elimination of dangling bonds.

The experiment conclusively demonstrates that $C_{12}Cl_8$, a perchlorinated fullerene intermediate predicted by Pentagon Road mechanism, can act as the growing species for fullerene formation. In addition to C_{60}, various perchlorinated carbon clusters were created from laser ablation of $C_{12}Cl_8$ as well. Information learned from the products is helpful to understand the mechanism of fullerene formation. Further investigation on the proposed process may open up a new pathway for the purpose. However, to verify the proposed mechanism, further experiments are still required, such as production of larger perchlorinated intermediates and characterization of their structures. The efforts are currently in progress.

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