

## Studies of the Formation of Carbon Clusters

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Experimental and theoretical studies focusing on the formation of carbon clusters are described. In the experiment on discharge in liquid chloroform, a series of perchlorinated fragments of C<sub>60</sub> was synthesized and a scarce amount of C<sub>60</sub> was detected. In the laser vaporization experiments, it was found that the production of C<sub>60</sub><sup>+</sup> and other fullerene ions could be promoted by doping chlorine-containing compounds into carbon targets. Chlorine atoms were found to play key roles of not only tying up the dangling bonds of the polycyclic carbon clusters, but also catalyzing the formation of fullerenes. The results showed that C<sub>60</sub> and other fullerenes are formed from growth of small carbon species and supported the "Pentagon Road" scheme of the fullerene formation mechanism. On the other hand, *ab initio* calculations were carried out on formation reactions of C<sub>60</sub> from its various perchlorinated fragments, C<sub>60-2m</sub>Cl<sub>10</sub>. The monotonically decreasing calculated energies of reactions with growing size of the fragments confirm that the formation reaction is energetically favorable.

**KEY WORDS:** Fullerene; formation mechanism; carbon cluster.

### INTRODUCTION

Study of carbon clusters has been a very active field, especially since the discovery and synthesis of macroscopic amounts of C<sub>60</sub> and other fullerenes [1, 2]. The hardest part of the study is to reveal the formation mechanism of the species [3–8]. Soon after their surprising discovery, Smalley and co-workers proposed an appealing mechanism which they dubbed the "Pentagon Road." The mechanism assumes that the lowest-energy structures for carbon clusters in the 25–50 range are open graphic cups [3–5]. Heath suggested the "Fullerene Road" scheme, which involves a growth mechanism

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similar to the Pentagon Road (addition of small carbon fragments), but the intermediates with 30–58 carbon atoms are closed to fullerene cages [6]. McElvany *et al.* have studied the formation and reaction of the cyclic carbon clusters  $C_{18}$ ,  $C_{24}$ , and  $C_{30}$ , and the result indicates that  $C_{60}$  formation can occur through ring coalescence and annealing of such medium-sized carbon clusters, rather than gradual addition of  $C_2$  and  $C_3$  particles [7, 8]. However, neither scheme can sufficiently account for all the experimental observations on the formation of fullerene molecules.

An effective way to reveal the mechanism is to trap the intermediate in  $C_{60}$  formation. Some of these experiments involve the addition of new reactants to the helium buffer gas during graphite vaporization. For instance, addition of cyanogen to the reaction leads to formation of polyynrods, capped by cyano groups [9]. In contrast, in the presence of a partial pressure of chlorine, a series of perchlorinated fullerene fragments was isolated [10]. In one of our recent experiments, the perchlorinated fullerene fragments were also synthesized by electrically discharging liquid chloroform. The trapped compounds are cup-shaped as predicted by the Pentagon Road scheme [11], but they are produced from  $C_1$  species rather than graphitic network. The observation suggests that  $C_{60}$  and other fullerenes may grow from  $C_2$  or even  $C_1$  species.

To verify the suggested scheme, we tried to produce  $C_{60}^+$  and other fullerene ions by direct laser vaporization, in a way somewhat different from Smalley's [1]. No buffer gas was introduced during the experiments. Various elementary carbons, such as graphite, amorphous carbon, glassy carbon, and even diamond, doped with different chlorine-containing compounds, were chosen as targets. The ions produced from the samples were analyzed by mass spectra. It was found in the experiments that fullerene ions could be produced from different carbon sources as long as some compounds were doped in the targets. The results are also informative for understanding the formation mechanism of  $C_{60}$  and other fullerenes.

In addition to the experimental studies, we also performed *ab initio* calculations on various  $C_{2n}Cl_{10}$  molecules that are perchlorinated intermediates of the Pentagon Road scheme. The theoretical results help to establish an overall picture of the formation process of  $C_{60}$ .

## EXPERIMENTAL

### Discharge Experiment in Liquid Chloroform

Figure 1 displays the reaction device of the liquid discharge experiment. In the experiment described here, chloroform was selected as both reagent

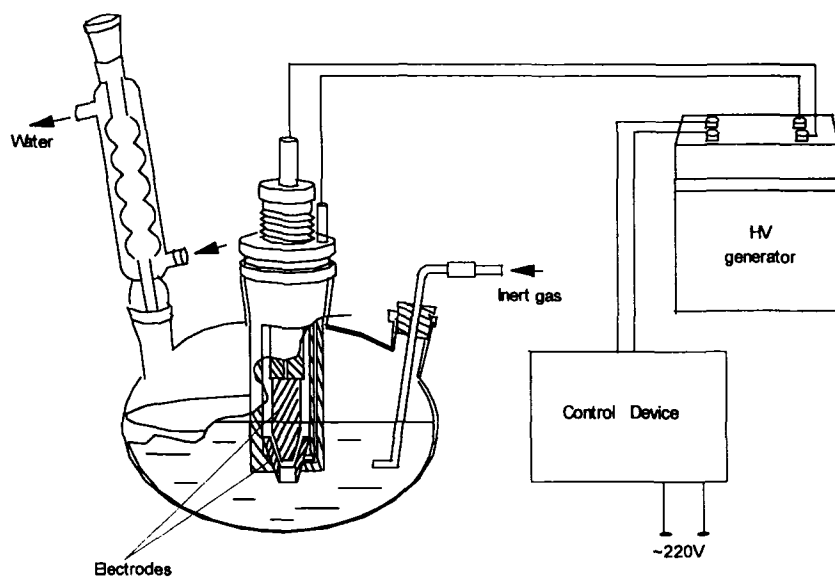


Fig. 1. Reaction device of the liquid discharge experiment.

and solvent. Five hundred milliliters of pure chloroform was bubbled with purified nitrogen gas to preserve an inert atmosphere in the device. In the experiment, the gap between the pair of copper electrodes was about 1 mm; a.c. power with a voltage over 10 V and a 20 Hz frequency was supplied to the electrodes. The stable arc discharge was maintained by adjusting the voltage or the electrode gap with an arc current of around 20–50 mA. During the reaction, large amounts of HCl and Cl<sub>2</sub> gas were released.

The discharge reaction in liquid chloroform was stopped after a 5-h discharge, and a deep red-brown solution was obtained. The products with a high vapor pressure were analyzed by GC-MS. After vaporizing the unreacted solvent, about 4 g of residue was collected. About 40% of the residue was sublimated at 160°C as colorless needle crystals which were characterized as hexachlorobenzene [11]. The remainder was dissolved in benzene and separated by neutral Al<sub>2</sub>O<sub>3</sub> column chromatography, with petroleum ether/benzene at different ratios as elute. Several fractions were collected, with different yields: light-yellow needle crystal, 8%; orange needle crystal, 20%; green feather crystals, 12%; and brown powder, 8%. The separated components were characterized by spectroscopy. The structures of two single crystals obtained were determined by X-ray diffraction with the Sir92 and Shelex 93 program package [13].

### Laser Vaporization Experiment

The time-of-flight mass spectrometer used in the experiment has been described in detail elsewhere [12], and hence only a brief description is presented here. The carbon cluster ions were produced by direct laser vaporization. The pulsed laser beam selected for the experiment was the second harmonic output of a quantum Nd:YAG laser and was gently focused with a lens ( $f = 80$  cm) to an approximately 1-mm spot on the sample with a power density of the order of  $10^8 \text{ W} \cdot \text{cm}^{-2}$ . During the experiment, the apparatus was pumped to a vacuum of  $2 \times 10^{-6}$  Torr, and no buffer gas was introduced to the system. The sample was located 6 cm away from the exit of the acceleration electrodes. The cluster ions were formed in the laser vaporized plasma and diffused into the acceleration region of the mass spectrometer by their initial kinetic energy.

The pulsed acceleration field of the mass spectrometer was applied at 950 V. After flying over a 2.5-m field-free drift tube, the ions with different masses were separated. The output ion signal from a microchannel-plate detector was recorded by a  $1 \times 10^8 \text{ s}^{-1}$  transient digitizer after preamplification. Under normal operating conditions, the mass resolution of the mass spectrometer is around 400.

The main features of the experiments are the extensive selection of the samples, pure or mixed species, as the target of the direct laser vaporization and doping of the samples with chlorine-containing compounds. The samples include elementary carbons with various structures: amorphous carbon, glassy carbon, graphite, and diamond. The samples also include various organic compounds, polymers, and even inorganic species.

Most of the samples are commercially available and are analytically pure except for the carbon powder, which is spectrally pure. The perchlorinated aromatic compounds were synthesized in our laboratory. Purity of the compounds was characterized by HPLC analysis.

### THEORETICAL

Standard *ab initio* molecular orbital calculations were carried out with the Gaussian 94 system of programs [14]. Geometry optimization and Hartree-Fock energies of various  $\text{C}_{2n}\text{Cl}_{10}$  as well as  $\text{C}_{60}$  and  $\text{C}_2$  were calculated at the HF/STO-3G level [15]. No symmetry constraint was applied in the calculations.

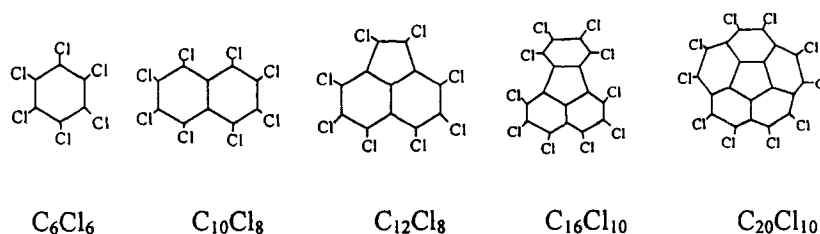
The energies of reactions  $\text{C}_{60-2m}\text{Cl}_{10} + m\text{C}_2 \rightarrow \text{C}_{60} + 10\text{Cl}$  ( $m = 4-20$ ) were obtained by subtracting the energy summations of reagents from that of products. The energies of reactions relative to that of  $\text{C}_{20}\text{Cl}_{10} + 20\text{C}_2 \rightarrow \text{C}_{60} + 10\text{Cl}$  were plotted as a function of the number of carbon atoms in  $\text{C}_{60-2m}\text{Cl}_{10}$ .

## RESULTS

### Synthesis of Perchlorinated Fragments of $C_{60}$ from Chloroform

Figure 2 displays the recorded gas chromatogram. From mass spectrometry analysis of each product separated by gas chromatography, components of the products can be determined and their structures suggested. The structural formula of each separated product is labeled above its chromatographic peak. The area of each peak is approximately proportional to the relative abundance of the related product. As shown in Fig. 2, among the products characterized by GC-MS, tetrachloroethylene, hexachlorobutadiene, and hexachlorobenzene are the most abundant.

The various components from column chromatography were identified as octachloronaphthalene, octachloroacenaphthylene, decachlorofluoranthene, and decachlorocorannulene, respectively [11]. Structures of the products are illustrated as below.



The compounds illustrated above account for about 90% of the total products. In addition, other products from the discharge reaction, such as  $C_{60}$  and larger perchlorinated polycyclic compounds, have been detected by mass spectrometry [16].

The X-ray diffraction results show that the obtained single crystals are perchloroacenaphthylene and perchlorofluoranthene [16], two polycyclic aromatic compounds containing a five-membered ring in the molecule. Their peripheral carbon atoms are saturated by chlorine. Perchlorofluoranthene is a twisted molecule including a five-membered ring in its center. Apparently, the molecule tends to curl up.

### Production of Fullerene Ions by Laser Vaporizing Carbon Targets Doped with Chlorine-Containing Compounds

In the experiments, various forms of carbon were chosen as target. The carbon cluster ions produced from a pure elementary carbon target are shown in the mass spectra in Fig. 3. Sizes of the observed cluster cations do not exceed 30 carbon atoms, and their signal intensities alternate in an interval of 4 atoms. The sizes and their distribution correspond to the

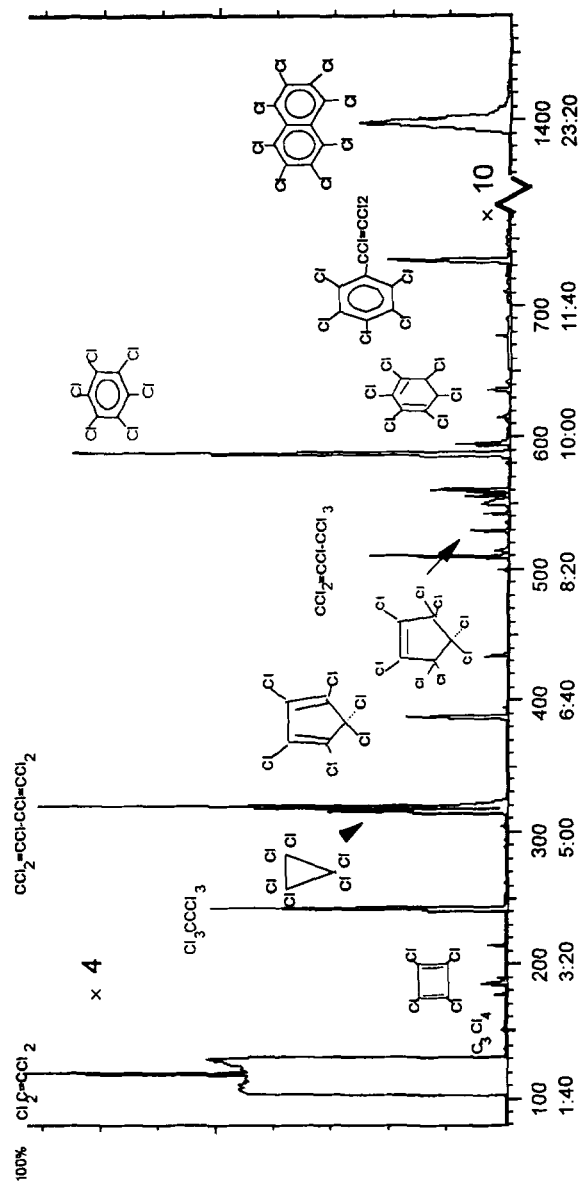
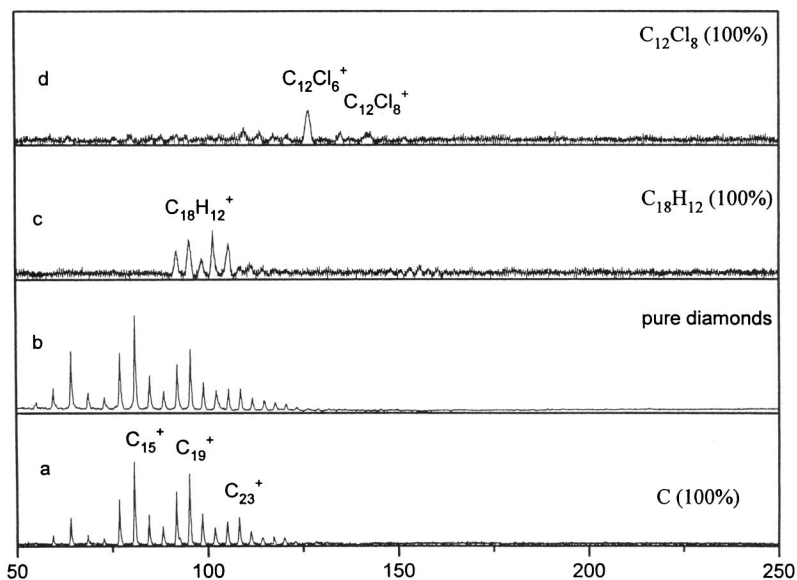


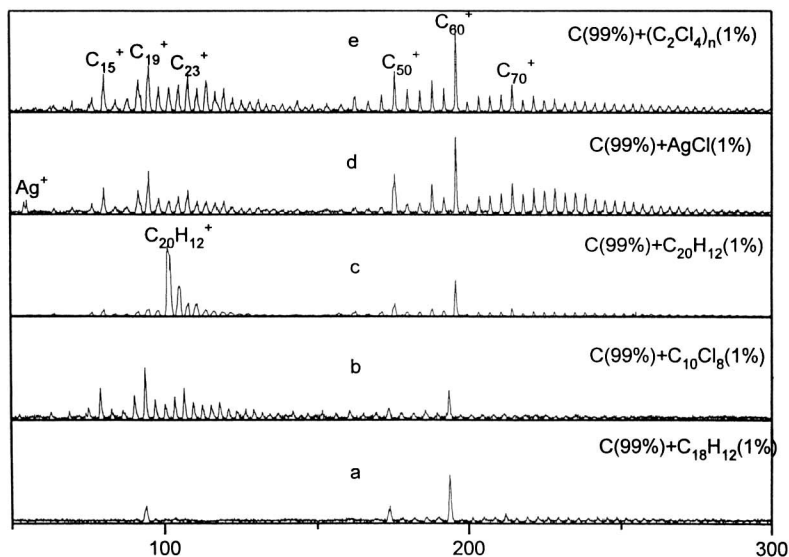
Fig. 2. Gas chromatogram of products with a high vapor pressure and their structural formula (labeled above chromatographic peaks) suggested from mass spectrometry analysis of each separated component.



**Fig. 3.** Time-of-flight mass spectra of cations produced by laser ablating the samples of amorphous carbon (a), pure diamonds (b), chrysene (c), and perchloroacenaphthylene (d).

cyclic structure of the carbon clusters [17–19]. The experiment has been repeated many times, varying either the power density or the vaporization time of the laser beam. As long as the sample is kept at a high purity, no  $C_{60}$  or other fullerenes ions can be produced from the sample. Mass spectra produced from some pure polycyclic compounds, such as chrysene and perchloroacenaphthylene, are also displayed in Fig. 3, and no fullerene ions can be observed in them either.

However, when the carbon target, such as amorphous carbon powder, was doped with polycyclic compounds, such as chrysene and perchloroacenaphthylene, a typical “fullerene mass spectrum” was observed as shown in Fig. 4. In the mass spectra,  $C_{60}^+$  exhibits an especially high signal intensity. The frameworks of both chrysene and perchloroacenaphthylene are fragments of  $C_{60}$ , and the latter even contains a five-membered ring, so it is reasonable to speculate that they might model the structure of the laser vaporized products. Similarly, it is found that the productions of  $C_{60}$  are promoted effectively by other compounds structurally unrelated to  $C_{60}$ , such as benzoapyrene ( $C_{20}H_{12}$ ), tetracyanoethylene [ $C_2(CN)_4$ ], and even various polymers such as polyvinyl chloride and polypropylene. Further experiments revealed that even some inorganic compounds such as AgCl and  $FeCl_3$ , which consist of chlorine atoms instead of carbon or hydrogen



**Fig. 4.** Time-of-flight mass spectra of cations produced by laser ablating the samples of C(99%) + C<sub>18</sub>H<sub>12</sub>(1%), (a) C(99%) + C<sub>10</sub>Cl<sub>8</sub>(1%) (b), C(99%) + C<sub>20</sub>H<sub>12</sub>(1%) (c), C(99%) + AgCl(1%) (d), and C(99%) + (C<sub>2</sub>Cl<sub>4</sub>)<sub>n</sub>(1%) (e).

atoms, can promote the formation of C<sub>60</sub> very significantly. Some of the recorded mass spectra are also displayed in Fig. 4, and a flagpole-like mass peak of C<sub>60</sub><sup>+</sup> is observed in the spectra.

After surveying the various additive compounds, we finally discovered that the promotion effect of the additive compounds does not come from their component carbon atoms but from other atoms or groups. Although the atoms or groups varied in the different additive compounds, the chlorine atom was found to be the most effective in our laser vaporization experiments.

To characterize the promotion mechanism of the additive compounds, one of the effective compounds, chrysene, was mixed into the carbon target at different ratios. Figure 5 displays mass spectra of positive ions produced from the samples in the same conditions. The figure shows that fullerene ions could be created only when chrysene was mixed in a relatively small amount. The less chrysene mixed in the target, the stronger the ion signal intensity of C<sub>60</sub><sup>+</sup>. Obviously, the mixed chrysene or other promoting compounds do not contribute clustering carbon atoms of fullerene ions, and they simply promote the formation of fullerenes as catalysts.

In addition to carbon powder, other elementary carbons, such as highly oriented pyrolytic graphite (HOPG), glassy carbon, and even diamond, have



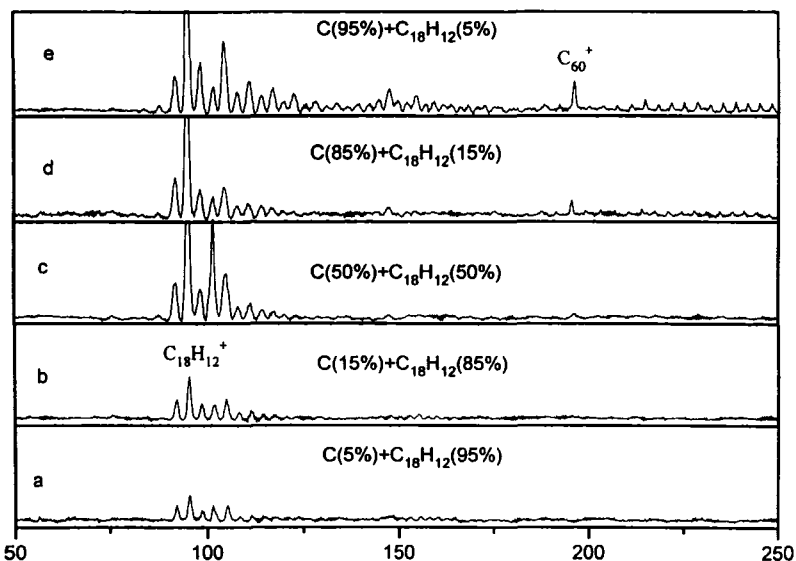


Fig. 5. Time-of-flight mass spectra of cations produced by laser ablating the samples of C(5%) + C<sub>18</sub>H<sub>12</sub>(95%), (a) C(15%) + C<sub>18</sub>H<sub>12</sub>(85%) (b), C(50%) + C<sub>18</sub>H<sub>12</sub>(50%) (c), C(85%) + C<sub>18</sub>H<sub>12</sub>(15%) (d), and C(95%) + C<sub>18</sub>H<sub>12</sub>(5%) (e).

also been selected as targets of laser vaporization. As revealed in the recorded mass spectra, C<sub>60</sub> and other fullerene ions can be produced from the carbon sample with different structures, as long as it is doped with a very small amount of the additive compounds.

In the discharge experiment, the products are bowl-shaped graphite cups whose dangling bonds are tied by chlorine atoms, such as C<sub>20</sub>Cl<sub>10</sub>. To test if the species can grow to fullerenes from the addition of C<sub>2</sub>, we mixed it with carbon powder at a 1:20 weight ratio. The ions generated from the target are quite complicated: in addition to the molecular ion peak, a series of bare and chloride carbon cluster ions, C<sub>n</sub>Cl<sub>10</sub><sup>+</sup> and C<sub>n</sub><sup>+</sup> (*n* = even number) was observed in the mass spectrum. Those clusters obviously grow from the C<sub>20</sub>Cl<sub>10</sub> precursor from the addition of C<sub>2</sub> provided by the carbon powder. As the clusters gather enough pentagons in the right places, they would be closed into a hollow cage by dissociating the chlorine atoms, thereby forming fullerenes.

#### *Ab Initio* Calculations on Perchlorinated Fragments of Fullerene

The STO-3G level optimized geometries of the main intermediates of the "Pentagon Road" mechanism are shown in Fig. 6. The Hartree-Fock energies of a series of C<sub>2n</sub>Cl<sub>10</sub> are listed in Table I.

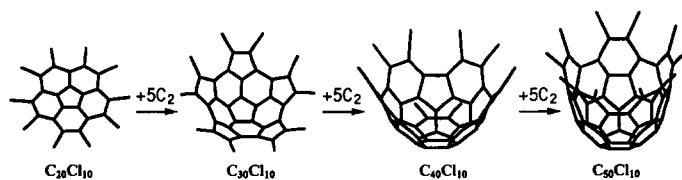


Fig. 6. STO-3G/HF optimized geometry for the main intermediates of the "Pentagon Road" mechanism for the formation of fullerene.

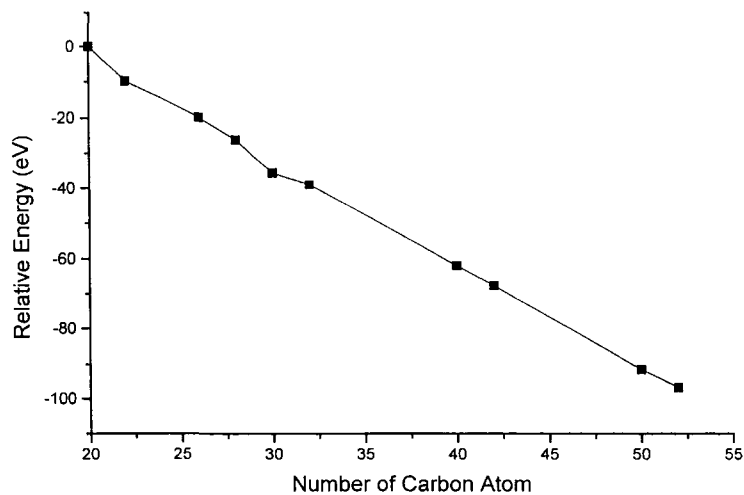


Fig. 7. *Ab initio* STO-3G/HF energies of the reactions  $C_{60-2m}Cl_{10} + mC_2$ , plotted as a function of the number of atoms in each perchlorinated intermediate.

Table I. The Hartree-Fock Energies of  $C_{2n}Cl_{10}$  and Relative Energies of the Reactions

Molecule	STO-3G energy (AU)	Relative energy of the reaction (eV)
$C_{20}Cl_{10}$	-5293.8448	0
$C_{22}Cl_{10}$	-5368.5099	-9.79
$C_{26}Cl_{10}$	-5518.1926	-19.78
$C_{28}Cl_{10}$	-5592.9792	-26.27
$C_{30}Cl_{10}$	-5667.7725	-35.57
$C_{32}Cl_{10}$	-5742.5610	-39.01
$C_{40}Cl_{10}$	-6041.8125	-62.09
$C_{42}Cl_{10}$	-6116.6228	-67.93
$C_{50}Cl_{10}$	-6415.8550	-91.54
$C_{52}Cl_{10}$	-6490.6904	-96.70
$C_{60}$	-2244.2212	
$C_2$	-75.0250	

Figure 7 is a plot of the relative energies of the reactions to  $C_{20}Cl_{10} + 20C_2 \rightarrow C_{60} + 10Cl$  as a function of the number of carbon atoms in the intermediate clusters. The energies decrease with increasing size of the intermediates.

The calculation results show that compounds, such as  $C_{30}Cl_{10}$ ,  $C_{40}Cl_{10}$ , and  $C_{50}Cl_{10}$ , a series of perchlorinated intermediates of the Pentagon Road scheme, are as stable as  $C_{20}Cl_{10}$ , which has already been synthesized and characterized in our experiments [11].

## DISCUSSION

### Carbon Clusters Formed from Growing-Up of Small Carbon Clusters

The experiments described in this article were performed in different environments and with different reactant materials, but their results revealed the same formation process:  $C_{60}$  and other carbon clusters can grow from one-carbon-containing species such as  $CHCl_3$  and  $CCl_4$ , which do not have to contain a six-membered ring.

The GC-MS results show that tetrachloroethylene, hexachlorobutadiene, and hexachlorobenzene are most abundant. One plausible explanation is that dichlorocarbene generated from chloroform aggregates to tetrachloroethylene, which dimerizes further to hexachlorobutadiene. A Diels–Alder reaction takes place between tetrachloroethylene and hexachlorobutadiene to form a six-membered ring. From the point of view of thermodynamics, the formation enthalpy of  $:CCl_2$  (296 J/mol) is more favorable than that of  $:CHCl$  (460 J/mol).

In the laser vaporization experiments, the carbon clusters were formed in laser plasma instead of in solution, and the starting species were different forms of elementary carbon. With the promotion effect of the additive compounds, however, all of them can produce fullerene ions by direct laser vaporization. Therefore, in the laser vaporized plasma, the elementary carbon sample must be completely fragmented to small carbon particles. Given an appropriate environment, the fragments can grow toward  $C_{60}$  and other fullerenes.

### Intermediate Carbon Clusters in Forming Fullerenes

The key to revealing the formation mechanism is to trap the intermediates involved in carbon cluster growth. In fact, all characterized products in the discharge of liquid chloroform can be considered as the perchlorinated intermediates in the process of forming  $C_{60}$ . Therefore, the

significance of the reaction is not just the synthesis of the decachlorocorannulene and other perchlorinated products, but also supporting "Pentagon Road" mechanism of fullerene formation.

The Pentagon Road scheme was proposed just after the discovery of  $C_{60}$ . The scheme assumes an open graphite cup as the intermediate [5]. Although the scheme offered an appealing explanation for the observed preferential formation of  $C_{60}$ , so far, there is no evidence for the existence of the curved graphite structure. However, some products characterized in the experiments, such as decachlorocorannulene ( $C_{20}Cl_{10}$ ), do have a cup-shaped structure. Though not all intermediates have been trapped in the experiments, formations of other intermediates are shown to be at least energetically favorable by *ab initio* calculation. As the clusters gather enough pentagons in the right places, they are closed into a hollow cage by dissociating the chlorine atoms.

Results of the laser vaporization experiments also favor the Pentagon Road scheme. In the experiments, chlorine atoms and other free radicals exhibited a remarkable catalytic effect in forming fullerenes, suggesting that the intermediate carbon clusters of fullerenes have dangling bonds. Comparing the mechanisms [3] suggested for fullerene formation, only the intermediates of the Pentagon Road scheme have dangling bonds.

Additional favorable results come from the *ab initio* calculations, in which the reactions from  $C_{2n}Cl_{10}$  to  $C_{60}$  by subsequent addition of  $C_2$  are considered. The steady decrease in the energies of reactions with increasing size of the perchlorinated intermediates suggests that the scheme is energetically favorable. Bates and Scuseria recently reported an energetic analysis of the principal intermediates of the Pentagon Road scheme and got similar results [20]. In their calculations, however, all intermediate carbon clusters have 10 dangling bonds, and the starting cluster, the bowl-shaped  $C_{20}$ , is less stable than its isomers. The problem does not exist in the intermediates considered in this study, because the chlorine atoms saturate the dangling bonds along the rim of the intermediate carbon clusters.

### Special Effect of Free Chlorine Atoms in Fullerene Formation

Chlorine atoms were involved in both discharge and laser vaporization experiments, but in different amounts. In the discharge experiment, the starting species is  $CHCl_3$  or  $CH_4$ , so the number of chlorine atoms involved in the reactions exceeds that of carbon atoms; but in the laser vaporization experiment, only a trace amount of chlorine-containing compound was doped into the carbon target. The effects of chlorine atoms in

the experiments were therefore different: in the laser vaporization experiment,  $C_{60}$  and other fullerenes are the predominant products; while in the discharge experiments, most products are perchlorinated polycyclic aromatic compounds. The different effects reveal the promotion mechanism of chlorine atoms in the process of fullerene formation.

In the laser vaporization experiments, free radicals were dissociated from the additive compounds by vaporization laser. The free radicals can react with carbon clusters and temporally stabilize the intermediate clusters by chemically tying up their dangling bonds. The bonded atoms or groups can also be dissociated in high-temperature plasma. Following the process of bonding and dissociation between the free radicals with the dangling bonds of the carbon clusters, the formation of  $C_{60}$  and other fullerene ions is promoted.

According to the suggested mechanism, the effective promoting species should be both a good binding species and a good leaving species with carbon clusters. As shown by our experimental results, free chlorine atom is the best species due to proper C-Cl bond strength. Since the chlorine atom simply reacts as a catalyst, a trace amount of the species is needed in the process of fullerene formation. Too many chlorine atoms in the environment will shift the bonding/dissociation equilibrium and hinder the formation of fullerenes.

## ACKNOWLEDGMENTS

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## REFERENCES

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley (1985). *Nature* **318**, 162.
2. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman (1990). *Nature* **347**, 354.
3. R. F. Curl and R. E. Smalley (1991). *Sci. Am.* **265**, 54.
4. R. E. Haufler, Y. Chai, L. P. F. Chibante, J. Conceicao, C. Jin, L. S. Wang, S. Maruyama, and R. E. Smalley (1991). *Mater. Res. Soc. Symp. Proc.* **206**, 627.
5. R. E. Smalley (1992). *Acc. Chem. Res.* **25**, 98.
6. J. R. Heath (1991). *ACS Symp. Ser.* **481**, 1.
7. S. W. McElvancy, M. M. Ross, N. S. Goroff, and F. Diederich (1993). *Science* **259**, 1594.
8. Y. Rubin, M. Kahr, C. B. Knobler, F. Diederich, and C. L. Wilkins (1991). *J. Am. Chem. Soc.* **113**, 495.
9. T. Grosser and A. Hirsch (1993). *Angew. Chem.* **105**, 1390.
10. T. Grosser and A. Hirsch (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 1340.

11. R. B. Huang, W. J. Huang, Y. H. Wang, Z. C. Tang, and L. S. Zheng (1997). *J. Am. Chem. Soc.* **119**, 5954.
12. R. B. Huang, Z. Y. Liu, H. F. Liu, Q. Zhang, C. R. Wang, L. S. Zheng, F. Y. Liu, S. Q. Yu, and X. X. Ma (1995). *Int. J. Mass Spectrom. Ion Proc.* **151**, 55.
13. G. M. Sheldrick, *SHELXL 93* (University of Göttingen, Göttingen, 1993).
14. R. L. Disch and J. M. Schulman (1986). *Chem. Phys. Lett.* **125**, 465.
15. For a general introduction to Hartree–Fock-based methods, see W. J. Hehre, L. Radom, P. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).
16. S. Y. Xie, R. B. Huang, L. H. Chen, W. J. Huang, and L. S. Zheng (1998). *J. Chem. Soc. Chem. Commun.* 2045.
17. G. von Helden, M. T. Hsu, P. R. Kemper, and M. T. Bowers (1991). *J. Chem. Phys.* **95**, 3835.
18. G. von Helden, M. T. Hsu, N. G. Gotts, and M. T. Bowers (1993). *J. Chem. Phys.* **97**, 8182.
19. G. von Helden, N. G. Gotts, and M. T. Bowers (1993). *Chem. Phys. Lett.* **212**, 241.
20. K. R. Bates and G. Scuseria (1997). *J. Phys. Chem.* **101**, 3038.