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Laser Productions of Fullerene Ions Promoted by Additive Compounds in Carbon Targets

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By doping various compounds, which can dissociate free radicals covalently bonding with carbon clusters, into the carbon target, C_{60}^+ and other fullerene ions were produced from direct laser vaporization. The compounds do not provide the carbon atoms, and to exhibit the promotion effect, only very small amounts of the species need to be doped, so the free radicals dissociated from the compounds behaved as catalysts in the formation process of the fullerenes. Among the various free radicals, free chlorine atom was found to be most effective in promoting fullerene formation. After doping the compounds, fullerene ions can be created from different forms of carbons, such as amorphous carbon, glassy carbon, graphite, and even diamond. Based on the experimental results, the catalysis mechanism of the free radicals and the formation process of fullerenes are suggested.

1. Introduction

Since the discovery and macroscopic synthesis of C_{60},[1,2] numerous experimental and theoretical attempts have been made to understand its formation mechanism of C_{60} and other fullerenes.[3−15] Smalley and co-workers proposed an appealing mechanism which they dubbed the “Pentagon Road”. The proposed mechanism offered an attractive explanation for the observed preferential formation of C_{60} from graphite vaporization, but there is no evidence for the existence of the curved graphitic intermediates.[16−18] Heath suggested the “Fullerene Road” scheme which involves a growth mechanism similar to the Pentagon Road (addition of small carbon fragments), but the intermediates with 30−58 carbon atoms are closed fullerene cages.[19] McElvany et al. studied the formation and reaction of the cyclic all-carbon molecules C_{18}, C_{24}, and C_{30}. Their result indicates that C_{60} formation can occur through ring coalescence and annealing of medium-sized carbon clusters, rather than sequential addition of C_2 and C_3 particles.[20,21] However, none of the proposed schemes can account for all observations about the growth of the 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, adding cyanogen to the reaction leads to the formation of polyyne rods that are capped by cyano groups.[22] In contrast, in the presence of a partial pressure of chlorine, a series of perchlorinated fullerene fragments were isolated.[32] In one of our recent experiments, the perchlorinated fullerene fragments were also synthesized by electrically discharging liquid chloroform.[23] The largest product characterized so far is decachlorocorannulene,[23] which is cup-shaped as predicted by the Pentagon Road scheme[16−18] but is produced from a C_1 species rather than a graphitic network. The observation suggests that C_{60} and other fullerenes may grow from C_2 or even C_1 particles.

C_{60} and other fullerene ions were first generated by laser vaporization of graphite target in the throat of a supersonic molecular beam nozzle and discovered in the recorded time-of-flight mass spectra as positive ions.[1] Production of C_{60}^+ was favored by the high density of He buffer gas around the target.[1] Recently, we tried to produce C_{60}^+ and other fullerene ions by direct laser vaporization. No buffer gas was introduced during the experiments. Various elementary carbons, such as graphite, amorphous carbon, glassy carbon, and even diamond, were chosen as the target, but it was doped with different compounds. The ions produced from the samples were mass analyzed. The results not only provide an efficient way to produce fullerenes from different carbon sources but also are informative for understanding the formation mechanism of C_{60} and other fullerenes.

2. Experimental Section

2.1. Instrumentation. The apparatus employed in this experiment has been described in detail elsewhere,[24] 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 is the second harmonic output of a Quantary Nd:YAG laser (532 nm wavelength, 7 ns pulse width) and was gently focused with a lens ($f = 80$ cm) to approximately a 1 mm spot on the sample with the power density on the order of 10^8 W cm^{-2}. During the experiment, the whole system was pumped to a vacuum of 2×10^{-6} Torr, and no gas was introduced into the system. The sample is located 6 cm away from the exit of the acceleration electrodes. Each time the sample was changed, the sample holder and the nearby sections of the apparatus were thoroughly cleaned to avoid the possible contamination. The cluster ions were formed in the laser-vaporized plasma and diffused into the acceleration region of the mass spectrometer by their initial kinetic energies.

The pulsed acceleration field of the mass spectrometer was applied at 950 V. After flying over a 250 cm field-free drift tube, the ions with different masses were separated. The output ion signal from the dual-microchannel-plate detector was digitized by a 100M sample s^{-1} transient digitizer after pre-amplification. Under normal operating condition, mass resolution of the apparatus can exceed 400.

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2.2. Samples. The main feature of the experiment is the extensive selection of the samples, pure or mixed species, as the target of the direct laser vaporization. The samples include elementary carbons with various structures, amorphous carbon, glassy carbon, graphite, and diamond, among which the amorphous carbon (carbon powder) sample is used most frequently. The structure of the carbon powder was characterized as microcrystals of graphite by Raman spectrometry and X-ray diffraction. The samples also include various organic compounds, polymers, and even inorganic species.

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

In the experiments, the elementary carbon, mostly amorphous carbon powder, was mixed with different compounds as the laser vaporization target. The various samples were directly vaporized by pulsed laser beam under the same experimental conditions. The carbon cluster ions produced by laser vaporization were recorded by time-of-flight mass spectra. Special attention was paid to the relative signal intensity of C_{60} and other fullerene ions in the recorded mass spectra.

3. Results

3.1. Laser Generation of C_{60} Significantly Promoted by Some Additive Compounds. Figure 1 displays the mass spectrum of carbon cluster ions produced from pure amorphous carbon powders (100%). Sizes of the observed cluster cations do not exceed 30 carbon atoms, and their signal intensity alternates in an order of 4. The sizes and the distribution correspond to the cyclic structure of the carbon clusters.[25−27] The experiment has been repeated many times by varying either the power density or ablation time of the laser beam. As long as the sample is kept in high purity, no C_{60} or other fullerenes ions can be produced from the sample.

However, if some polycyclic aromatic compounds, such as chrysene and perchloroacenaphthylene, were mixed with the carbon powders, a typical “fullerene mass spectrum” could be observed and was also shown in Figure 1. In the mass spectra, C_{60}^+ exhibits special high signal intensity. In the experiments, C_{60} was generated as soon as the mixed samples were ablated by the laser beam. Thus, the possibility can be excluded that structure or composition of the mixed sample was modified after the ablation.

Molecular skeletons of the additives, $C_{18}H_{12}$ or $C_{12}Cl_8$, are composed of carbon atoms, so it is possible that the fullerene ions were produced from coalescence and carbonation of the aromatic compounds. Hence, in the experiments, the pure $C_{18}H_{12}$ or $C_{12}Cl_8$ samples were ablated by the pulsed laser beam. As shown in Figure 1, no fullerene ions can be observed as the products of laser vaporization. Therefore, under the condition of direct laser vaporization, the fullerene ions can only be produced from a mixture of the amorphous carbon and the polycyclic aromatic compounds.

Both the amorphous carbon and the polycyclic aromatic compounds, chrysene, are composed of carbon atoms. To distinguish the source of carbon atoms forming the fullerenes, they were mixed with different ratios, and mass spectra of positive ions produced from the samples in the same conditions are shown in Figure 2. As illustrated in the figure, the fullerene ions can be created only when chrysene was mixed in a relatively small amount, and the less chrysene mixed in the target, the more remarkable the ion signal intensity of C_{60}^+ shown in the recorded mass spectra. Obviously, the mixed chrysene or other aromatic compounds do not contribute the clustering carbon atoms of the fullerene ions, and they simply promote the formation of the fullerenes as catalysts.

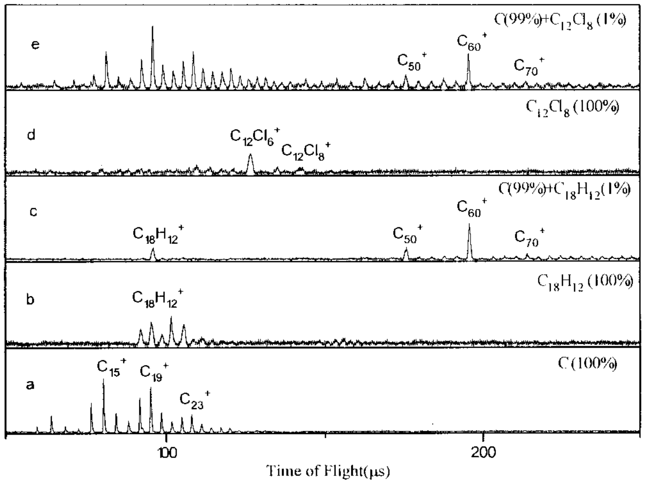

Figure 1. Time-of-flight mass spectra of cations produced by laser ablating the samples of amorphous carbon (a), $C_{18}H_{12}$ (b), mixture of C (99%) + $C_{18}H_{12}$ (1%) (c), $C_{12}Cl_8$ (d), and mixture of C (99%) + $C_{12}Cl_6$ (1%) (e). Here C symbolizes the amorphous carbon.

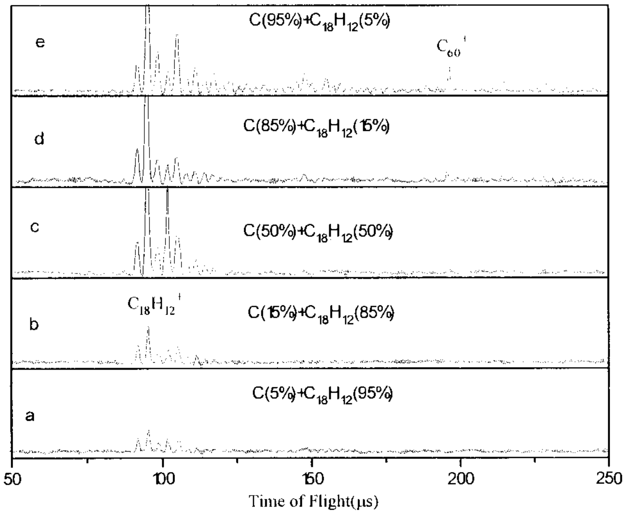

Figure 2. Time-of-flight mass spectra of cations produced by laser ablating the samples of C (5%) + $C_{18}H_{12}$ (95%) (a), C (15%) + $C_{18}H_{12}$ (85%) (b), C (50%) + $C_{18}H_{12}$ (50%) (c), C (85%) + $C_{18}H_{12}$ (15%) (d), and C (95%) + $C_{18}H_{12}$ (5%) (e).

3.2. The Promotion Effect and Structures of Additive Compounds. The framework of both additive compounds, chrysene and perchloroacenaphthylene, are the 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. To examine whether the structures of the additive compounds can affect the C_{60} formation, other aromatic compounds whose structures are unrelated to C_{60}, such as benzo[*a*]pyrene, $C_{20}H_{12}$, and hexachlorobenzene, C_6Cl_6, and other organic compounds, such as poly(vinyl chloride) and polypropyrene, were also selected and doped to the carbon powder sample in the laser vaporization experiments. As a matter of fact, all these organic compounds were found to be effective in promoting C_{60} formation, if their content in the target is in a very small amount (<1%). Some of the recorded mass spectra of the laser-vaporized products are displayed in Figure 3, and the mass peak of C_{60}^+ is shown in the spectra like a flagpole.

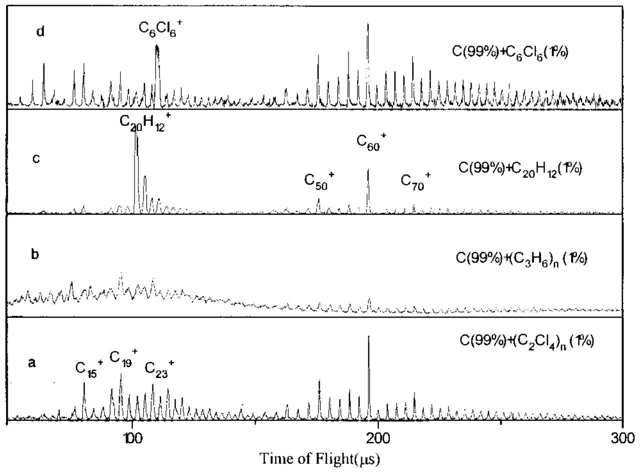

Figure 3. Time-of-flight mass spectra of cations produced by laser ablating the samples of C (99%) + $(C_2Cl_4)_n$ (1%) (a), C (99%) + $(C_3H_6)_n$ (1%) (b), C (99%) + $C_{20}H_{12}$ (1%) (c), and C (99%) + C_6Cl_6 (1%) (d).

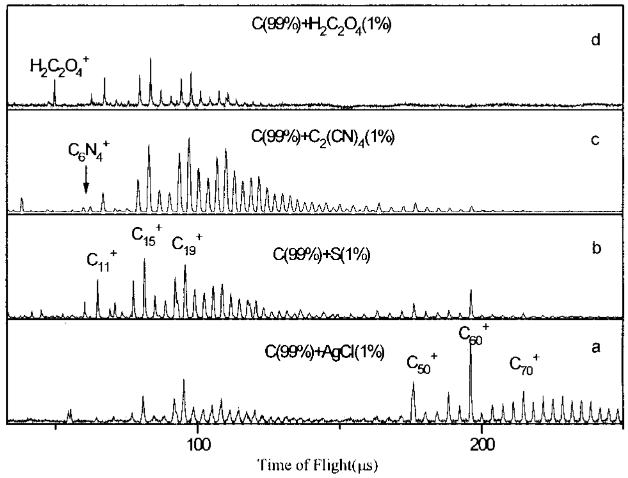

Figure 4. Time-of-flight mass spectra of cations produced by laser ablating the samples of C (99%) + AgCl (1%) (a), C (99%) + S (1%) (b), C (99%) + $C_2(CN)_4$ (1%) (c), and C (99%) + $H_2C_2O_4$ (1%) (d).

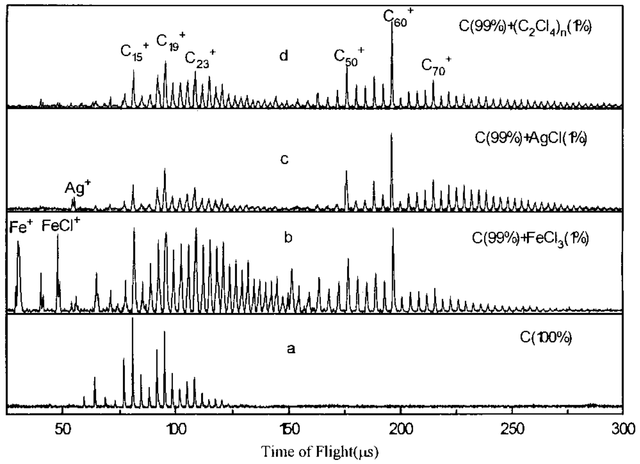

Figure 5. Time-of-flight mass spectra of cations produced by laser ablating the samples of C (100%) (a), C (99%) + $FeCl_3$ (1%) (b), C (99%) + AgCl (1%) (c), and C (99%) + $(C_2Cl_4)_n$ (1%) (d).

Thus, our experimental results reveal that, under the conditions of the direct laser vaporization, almost all of the organic compounds can promote the formation of C_{60}^+ and other fullerene ions. However, the compounds do not provide the clustering carbon atoms of the fullerenes, and even their structures cannot be correlated to the promotion effect.

3.3. The Promotion Effect and Component Atoms or Groups of the Additive Compounds. The additive compounds described above are organic compounds with hydrogen or chlorine atoms bonded with the carbon framework. Further experiments, however, revealed that not all carbon-containing compounds exhibit the promotion effect. Some carbon-containing inorganic compounds, such as $H_2C_2O_4$ and Na_2CO_3, cannot promote the formation of the fullerenes, but some inorganic compounds such as AgCl and $FeCl_3$, which consist of a chlorine atom instead of a carbon atom, can promote the formation very significantly. The effective additive compounds include organic compounds that do not contain H or Cl, such as tetracyanoethene, $C_2(CN)_4$, or inorganic materials such as elementary sulfur. Figure 4 displays selected mass spectra produced from the doped carbon powder samples.

After surveying the various additive compounds that were doped to the amorphous carbon powder as the laser-vaporizing targets, 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 atom or group varied in the different additive compounds, the chlorine atom was found to be most effective in our laser vaporization experiments. The difference can be perceived in Figure 4 by comparing the size distribution of carbon clusters in the different mass spectra.

3.4. The Promotion Effect and Chemical Bonding of Additive Compounds. In addition to the additive compounds mentioned above, our experiments have examined various organic and inorganic species that were doped to the carbon powder as the target of laser vaporization. Among them, only a few atoms or groups of the species were found to exhibit the promotion effect. For instance, none of the metals, whose powder was mixed with the carbon powder in the experiment, can promote the fullerene formation. The chlorine atom of the additives was found to be most effective in promoting the fullerene formation, but the pure ionic chlorine-containing compounds such as NaCl and KCl did not exhibit the effect at all. Figure 5 compared the mass spectra of positive ions produced from the carbon powder sample doped with different chlorine-containing compounds. After the comparison, one can find that the relative intensity of C_{60}^+ among the carbon cluster ions can be correlated to the covalence bonding of the chlorine atoms, so the promotion effect is the result of the bonding ability of the chlorine atom with the carbon atoms. In fact, the promotion effect of other additive compounds can also be attributed to the bonding ability of their component atoms or groups with the carbon atoms.

3.5. Production of Fullerene Ions from Different Forms of Carbon Doped with Additive Compounds. In the laser vaporization experiments described above, the additive compounds were doped to the carbon powder, which is characterized as the microcrystal of the graphite and may provide six-member rings for the formation of the fullerenes. To further characterize the promotion effect and process, the effective additive compounds such as poly(vinyl chloride) or AgCl was doped into other forms of carbon, glassy carbon, and even diamond, as the target of laser vaporization. The recorded mass spectra are displayed in Figure 6. As shown in the spectra, under the conditions of direct laser vaporization, C_{60} and other fullerene ions can be produced from the carbon sample with different structures, as long as it is doped with very small amounts of the additive compounds.

3.6. Production of Negative Carbon Cluster Ions with the Promotion of Additive Compounds. In the experiments,

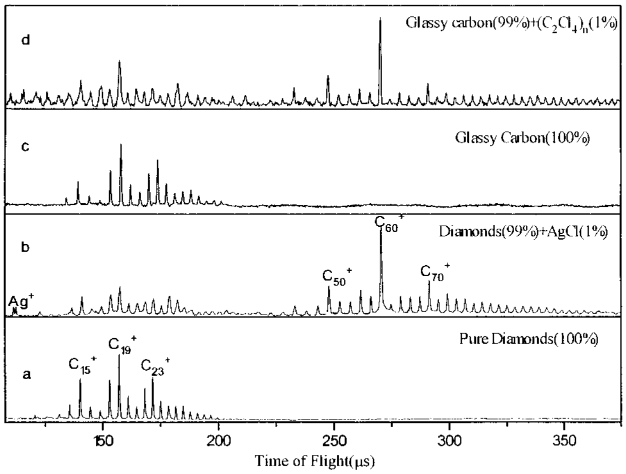

Figure 6. Time-of-flight mass spectra of cations produced by laser ablating the samples of diamonds (100%) (a), diamonds (99%) + AgCl (1%) (b), glassy carbon (100%) (c), and glassy carbon (99%) + $(C_2Cl_4)_n$ (1%) (d).

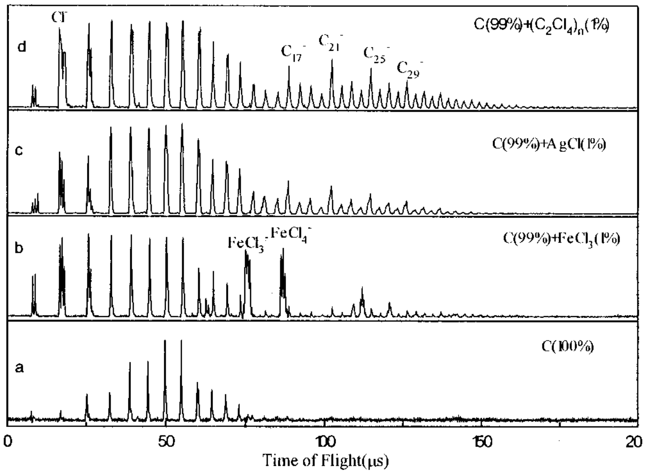

Figure 7. Time-of-flight mass spectra of cations produced by laser ablating the samples of C (100%) (a), C (99%) + $FeCl_3$ (1%) (b), C (99%) + AgCl (1%) (c), and C (99%) + $(C_2Cl_4)_n$ (1%) (d).

negative ions produced from the laser vaporization were also mass analyzed. Figure 7 displays some of the recorded mass spectra. Among them, Figure 7a shows the products created from the pure carbon powder, while other mass spectra in the figure were generated from the doped samples. None of the fullerene anions can be observed in the mass spectra. Comparing the mass spectra, however, one can notice that sizes of the carbon cluster anions increase significantly after the carbon sample was doped with the additive compounds such as $(C_2Cl_4)_n$ and AgCl, which were found to be effective in promoting the fullerene formation: Cluster anions produced from pure carbon powder are quite small, and their signal intensity exhibits even/odd alternation. The size distribution is characteristic of linear carbon clusters.[28,29] In contrast, sizes of the cluster cations created from the doped sample can exceed 40 carbon atoms, and their signal intensity alternates in an order of 4. The distribution corresponds to the cyclic structure of the carbon clusters.[28,29] Thus, growth of positive and negative cluster ions can be promoted by Cl, H, and other atoms or groups that can form covalent bonds with the carbon atoms, although formation of fullerene anions was not observed in the experiments.

4. Discussion

4.1. Promotion Mechanism of Additive Compounds. In the laser vaporization experiments reported in this paper, formation of fullerene ions was promoted by chlorine, hydrogen, and other free radicals that can form covalent bonds with carbon atoms. The free radicals were dissociated from the additive compounds by the vaporization laser. In contrast to the effect of the helium buffer gas, the additive compounds only need to be doped in a very small amount. Therefore, though both the helium atoms and the free radicals are not involved in the compositions of the fullerenes, their functions in promoting the formation of fullerenes are very different. The helium atoms are just the buffer gas, which cools the intermediate carbon clusters so that they can further grow and finally be annealed to the fullerenes. The free radicals can react with the 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 the high-temperature plasma. Following the process of bonding and dissociation between the free radicals and the intermediate carbon clusters, formation of C_{60} and other fullerene ions is promoted.

TABLE 1

bond	C≡C	C=C	C−C	C−H	C−F	C−Cl	C−Br	C−I
ΔH/kJ mol^{-1}	837	612	348	412	484	338	276	238

According to the suggested mechanism, the effective promoting species should be both a good binding species and a good leaving species with the carbon clusters. As shown by our experimental results, the free chlorine atom is the best species due to the proper C−Cl bond strength, which can be qualified from the comparison of C−C and C−X bond strengths shown in Table 1. Since the chlorine atom simply reacts as catalyst, only a trace amount of the species is needed in the formation process of fullerenes. Too many chlorine atoms in the environment will shift the bonding/dissociation equilibrium so that the chlorinated carbon clusters cannot grow to the fullerenes.

It has been reported that fullerene ions can be produced from direct laser vaporization of polymers.[30] Production of the fullerenes is enhanced by higher fluency and longer ablation time of the vaporization laser, and their yield was found to be preferable to the standard graphite laser vaporization source.[30] In fact, the production process may follow a similar mechanism: The polymer sample was mostly carbonized by the high fluency of laser beam, and the residual hydrogen atoms of the sample promoted the fullerene formation as observed in our experiments.

4.2. Formation Mechanism of Fullerenes Suggested by the Experiments. In the milestone experiment carried out by Kroto et al.,[1] helium buffer gas was introduced into laser vaporization source, and they found that production of fullerenes were favored by higher pressure of helium gas around the sample.[1] In our experiments, however, the carbon cluster ions were created by direct laser vaporization in high vacuum, and production of the fullerene ions was promoted by a very small amount of additive compounds doped to the carbon sample. In addition, with the promotion effect of the additive compounds, other elementary carbons with very different structures, such as diamond and glassy carbon, can produce fullerene ions by the direct laser vaporization. The experimental results not only provide an efficient way to produce C_{60} and other fullerenes but also reveal their growth process: C_{60} and other fullerenes can be formed from small carbon particles, which do not have to contain a six-member ring and may be as small as C_2. Therefore, in the laser-vaporized plasma, the elementary carbon sample is completely fragmented. Given an appropriate environment, the fragments can grow toward C_{60} and other fullerenes.

In the laser vaporization experiments, C_{60}^+ and fullerene ions can be produced from any form of carbon, so long as the carbon

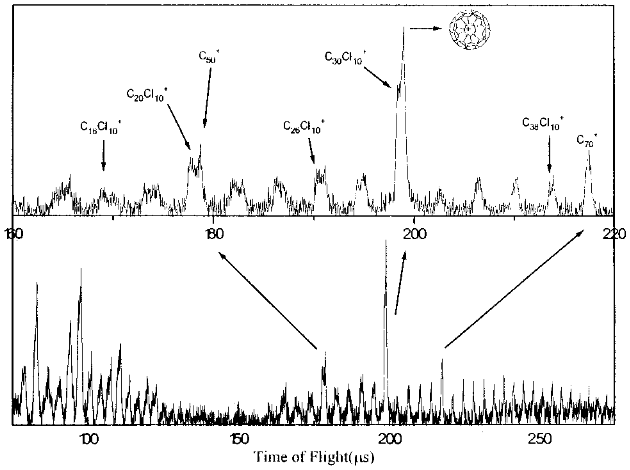

Figure 8. Time-of-flight mass spectra of cations produced by laser ablating the mixture of C (95%) + $C_{20}Cl_{10}$ (5%).

sample is doped with the additive compounds. The remarkable promotion effect of the species suggests that the intermediate of fullerenes have more dangling bonds than the small carbon clusters in ring or linear geometry. The observation seems to favor the "Pentagon Road" mechanism which assumes the open graphite cup as the intermediate.[16-18] However, though the scheme offered an attractive explanation of the observed preferential formation of C_{60}, so far there is no evidence for the existence of the curved graphite structure.

As a matter of fact, a bowl-shaped graphite cup with tied dangling bonds, decachlorocorannulene ($C_{20}Cl_{10}$), was synthesized in our recent arc experiment.[23] To test whether the species can grow to the fullerenes by adding C_2, we mixed the compound with carbon powder in a 1:20 weight ratio as the target of laser vaporization. Figure 8 displays the mass spectrum produced from the mixed sample. In addition to the molecular ion peak of $C_{20}Cl_{10}^+$, a series of bare and chloride carbon cluster ions, $C_nCl_{10}^+$ and C_n^+ (n = even number), were observed in the mass spectrum. Those clusters obviously grow from the $C_{20}Cl_{10}$ precursor after adding C_2 provided by the carbon powder.

The scheme was supported by the result from one of our recent experiments. In the experiment,[31] small carbon particles vaporized from the graphite target by a pulsed laser beam reacted with CCl_4 vapor, and the products finally stabilized in CCl_4 solution. After 20 h reaction, about 1 g of products was obtained. Other than the perchlorinated aromatic compounds, which have been characterized in the previous experiments, C_{60} and other fullerene products were also detected.[31] The results suggest that the perchlorinated aromatic compounds, some of which have the bowl-shaped graphite cup structures, might be the intermediates of fullerenes.

The suggested formation mechanism is similar to the Pentagon Road proposed by Smalley et al.,[16-18] only differing in the growth environments of the fullerenes. The Pentagon Road is based on the experiments performed in the helium buffer gas which allows the carbon clusters to find the energy minimum among structures. In the laser vaporization experiments reported in this paper, the intermediate clusters, especially the open graphitic cup intermediates, were stabilized by the chlorine atoms which can tie up the dangling bonds of the clusters. Figure 9 illustrates the suggested mechanism, in which the chlorine atoms dissociated from the doped species promote formation of C_{60} and other fullerenes as catalysts. Though the presence of chlorine radicals may change the relative stability of the intermediates so as to vary the growth mechanism of the carbon clusters, the results are still informative for understanding the formation mechanism of the fullerenes.

4.3. The Difference between Positive and Negative Carbon Cluster Ions. In our experiments, growths of both positive and negative cluster ions were found to be promoted by the additive compounds, but their promotion effects are different: C_{60} and other fullerenes can be produced as positive ions, but the produced negative ions were limited to those with ring structures. In fact, if the pure polycyclic hydrocarbons were selected as the sample of laser vaporization, carbon cluster anions with sizes over 200 atoms can be produced. The mass spectrum shown in Figure 10 is an example. The large carbon cluster anions appearing in the mass spectrum are composed of even number of atoms only, which is one of the characteristic of the fullerenes. However, C_{60}^- as well as C_{70}^- does not exhibit the prominent signal intensity as observed in the mass spectra of positive ions. The previous study already reveals that the Buckminsterfullerene only represents ~20% of the C_{60}^-

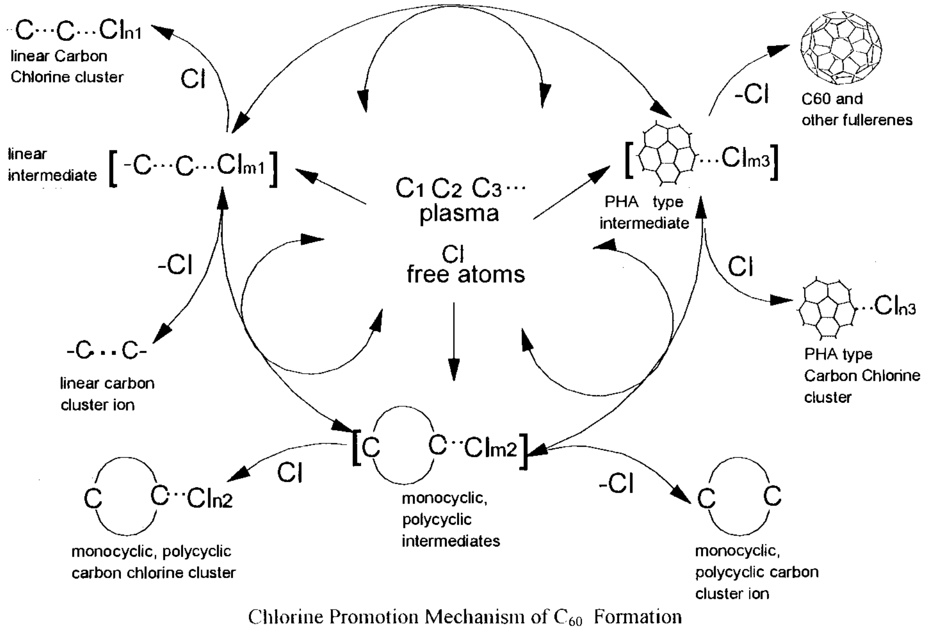

Figure 9. Suggested formation mechanism of fullerenes catalyzed by AgCl doped in carbon targets.

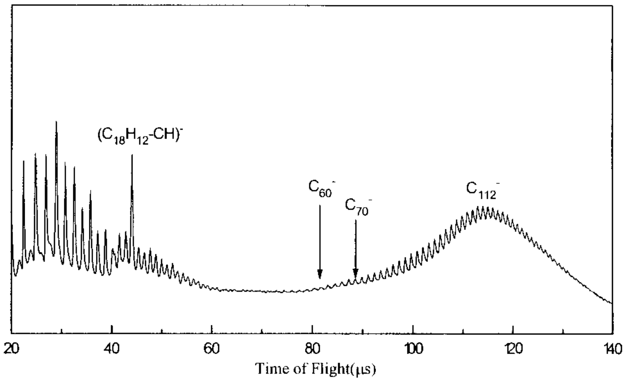

Figure 10. Time-of-flight mass spectra of anions produced by laser ablating the chrysene ($C_{18}H_{12}$) sample.

composition, and large planar rings are the dominant species of the carbon cluster anions.[29] Therefore, the promotion effect does not depend on the charge state of the clusters. The difference between the positive and negative charged products observed in the experiments is due to the different structures dominating in the large cluster cations and anions.

Our experiments have not yet involved the neutral species, but from the results of the cluster cations and anions, one can expect that growth of the neutral carbon clusters can be promoted with the appropriate additive compounds as well. We are also trying to apply the promotion effect to the synthesis of fullerenes in a macroscopic amount. The experiment is still in progress.

5. Conclusions

1. Under the conditions of direct laser vaporization, formation of fullerene ions can be promoted with some compounds that were mixed into the carbon sample. With the promotion of the additive compounds, fullerene ions can be produced from different forms of carbons, such as amorphous carbon, diamond, glassy carbon, and graphite. To exhibit the promotion effect, only very small amounts of the additive compounds were needed to mix with the carbon sample.

2. The promotion effect of the additive compounds is attributed to Cl, H, CN, and other free radicals that were dissociated from the compounds by the vaporization laser. The free radicals tie up dangling bonds of the carbon clusters and help stabilize the intermediates for forming the fullerenes. Among the various free radicals, the chlorine atom was found to be most effective for the promotion, which can be attributed to the proper C−Cl bond strength. Following the process of bonding and dissociation between the free radicals with the dangling bonds of the carbon clusters, formation of C_{60} and other fullerene ions is catalyzed.

3. Our experimental results confirm that C_{60} and fullerenes can grow from very small carbon particles that do not have to be rings or fragments of the fullerenes. The results favor the mechanism of the Pentagons Road; i.e., the growth of C_{60} and other fullerenes follows the addition of C_2 and other small carbon particles to the reactive edges of the developing graphite network.

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