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In Situ Synthesis of Chlorinated Fullerenes by the High-Frequency Furnace Method

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Exohedrally chlorinated fullerenes have been synthesized by in situ chlorination using the high-frequency furnace method in the presence of carbon tetrachloride as reagent. In addition to the previously reported chlorinated non-IPR (isolated pentagon rule) fullerene cages of $C_{2n}Cl_{2m}$ (n = 25, 27, 28, 30, 32 and 33, m = 2–6), a C_{68} and various new higher fullerenes including $C_{2n}Cl_{2m}$ with n = 36, 37 and 39 were present in the soot extracts in significant quantities, as shown by HPLC/off-line mass spectrometric analyses. A more detailed analysis showed the presence of several species with the same carbon content that could arise from either the formation of different isomers or different degrees of chlorination.

Introduction

Fullerenes are an extended family of spherical carbon cage molecules that continue to attract considerable attention from the scientific community because of their remarkable properties and potential applications. Despite intense research during the last 25 years, only a small fraction of all the possible members of this family has been synthesized and an even smaller number has been isolated and characterized. This also holds true for the stable cages that obey the so-called isolated pentagon rule (IPR), which states that all pentagons have to be completely surrounded by hexagons.[1] Indeed, all the known empty fullerenes obtained by various methods of graphite evaporation, namely laser ablation, arc-discharge or inductive heating, obey this rule without exception.[2–4] However, the fullerenes that satisfy the IPR represent only a tiny fraction of the possible fullerene isomers that in principle may be formed. For instance, there is only one IPR cage of C_{60} in contrast to 1811 non-IPR isomers and the non-IPR/IPR ratio surges exponentially with increasing number of carbon atoms in the cage.[1] The fullerene species C_{2n} with $n < 35$, excluding C_{60}, do not have IPR structures and therefore have not been accessible experimentally for a long time. To access these species, which all exhibit fused pentagons in their carbon cages, either endo- or exohedral stabilization during the synthesis process is necessary.[5] In recent years it has been shown that in situ chlorination during the synthesis in an arc-discharge reactor leads to the formation of various stable chlorinated non-IPR fullerene species. Since the first report on such a species, $C_{50}Cl_{10}$, in 2004 several others have been isolated and characterized, namely $C_{54}Cl_8$, $C_{56}Cl_8$, $C_{56}Cl_{10}$, $C_{60}Cl_8$, $C_{60}Cl_{12}$, $C_{64}Cl_4$, $C_{66}Cl_6$ and $C_{66}Cl_{10}$.[6–10] However, no higher, in situ synthesized chlorinated fullerene species have been reported so far and all chlorinated derivatives of IPR higher fullerenes have been synthesized by the chlorination of stable IPR fullerenes.[11–16] Very recently Ioffe and coworkers reported on the possibility of chlorine stabilization of non-classical higher fullerene cages obtained by the rearrangement of the IPR carbon network during chlorination.[17,18]

The high-frequency furnace (HF furnace) method developed by our group presents an attractive alternative method for effective fullerene as well as endohedral fullerene production.[4,19] In contrast to the widely used arc-discharge method, the HF furnace is based on the evaporation of solid carbon by inductive heating in the absence of an electric arc. Therefore considerably less UV radiation is emitted which has been shown to be unfavourable for fullerene synthesis.[20] Furthermore, the HF furnace set-up provides milder synthesis conditions and good control over synthesis parameters such as carrier gas flow, pressure and carbon evaporation temperature.

In this paper we report the effective synthesis of chlorinated fullerenes by the HF furnace method. Notably, in addition to previously reported fullerenes (C_{50}–C_{66}), we have produced several new fullerene species including new higher fullerenes in exceptionally high yields. For instance, chlorinated C_{68}, C_{72} and C_{74} species were obtained, which are not contained in normal fullerene extracts. MS analysis of several fractions, which were extracted from the raw soots and separated by HPLC, further revealed that certain fullerenes (including the already mentioned C_{68}, C_{72} and C_{74}) are present in more than just one fraction. This indicates the

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formation of either different isomers (including different chlorination patterns) or fullerenes with different degrees of chlorination.

Results and Discussion

Halogenated and non-halogenated fullerenes were obtained by the evaporation of a solid carbon source by inductive heating using the high-frequency furnace method in the presence of carbon tetrachloride as reagent. The carbon tetrachloride decomposes when passing through the hot zone (see Figure 1). The presence of CCl_4 results in the formation of brownish soots (from now on termed as in situ chlorinated fullerene soots, ICF soots), which differ notably in colour from the pitch-black fullerene soots produced in the absence of CCl_4 (known as empty fullerene soots, EF soots; see the Supporting Information for details). The cold extraction of ICF soot with toluene results in a yellow-brown solution in contrast to the dark-red colour of the EF extract. The ICF soot contains a remarkably bigger soluble fraction in comparison to EF soot. Thus, only 10–20 wt.-% can be extracted from the latter in the best case, whereas ICF soot typically contains 50–70 wt.-% of extractable material. LDI mass spectrometric analysis shows a significantly different distribution of fullerene species in the EF and ICF toluene extracts obtained under otherwise identical experimental conditions (Figure 2). As expected, no fullerenes smaller than C_{60} or between C_{60} and C_{70} are observed in the EF extract because they do not have IPR structures and do not form under the synthesis conditions in the HF furnace. In contrast, signals corresponding to such empty and chlorine-free, exotic non-IPR fullerenes are clearly observable in the ICF extract. Clearly, these latter fullerene species need to be derivatized with chlorine to be stable and soluble.

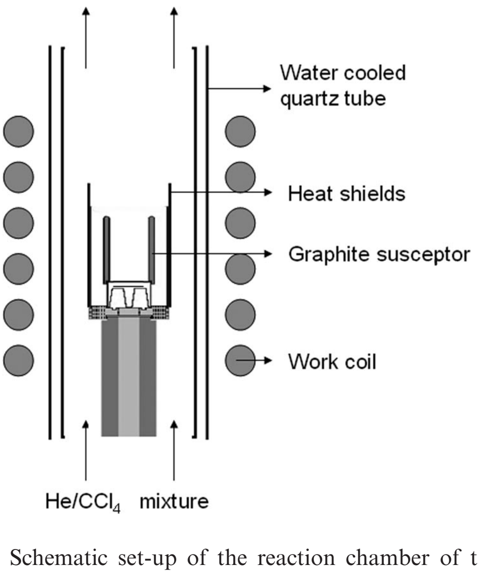

Figure 1. Schematic set-up of the reaction chamber of the high-frequency furnace.

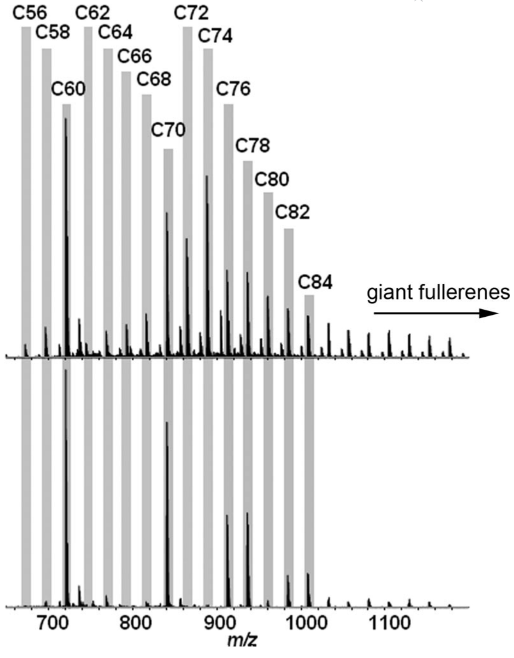

Figure 2. Mass spectra of the toluene extracts of in situ chlorinated fullerene soot (top) and empty fullerene soot (bottom; positive mode). Grey bars only serve as guides for the eye.

Therefore the observed signals have to stem from fullerenes stripped of their chlorine atoms by the laser desorption process during MS detection, which is a well-known phenomenon.[21–25] Indeed, a closer inspection reveals weak signals corresponding to residual chlorinated fullerene species (see the Supporting Information for details). The intensities of the peaks decrease in the order $C_{60} > C_{70} > C_{76}/C_{78} > C_{82}/C_{84}$ and $C_{60} > C_{74} > C_{70} > C_{72} > C_{76}/C_{78} > C_{80} > C_{82} > C_{68}/C_{84} > C_{56},C_{58},C_{62},C_{64},C_{66}$, for the EF and ICF extracts, respectively. In addition, the MS analysis of the ICF extract shows unusually high intensities of the giant fullerenes, which can be barely observed in the EF extract at all. Remarkably, the signals of C_{72} and C_{74}, which are completely absent in the EF extract, have extremely high intensities that are comparable to, or even higher than, C_{70} (Figure 2). Both C_{72} and C_{74} have only one IPR isomer but have never been observed in soot extracts as pristine molecules. It has been suggested that the IPR isomer of C_{72} does not form because of high local molecular strain,[26,27] whereas IPR C_{74} has been found in fullerene soot previously[28,29] but is not soluble due to a very small HOMO–LUMO gap.[30] Hence the signals observed for the ICF extract correspond either to IPR or non-IPR isomers stabilized by chlorine atoms. The intermediate chlorine derivatization is also confirmed by the observation of peaks corresponding to $C_{72}Cl$ and $C_{74}Cl$ species (see the Supporting Information). In addition to fullerenes, several chlorinated polycyclic aromatic hydrocarbons (PAHs) like $C_{12}Cl_8$, $C_{18}Cl_{10}$, $C_{20}Cl_{10}$, $C_{22}Cl_{10}$ and $C_{24}Cl_{10}$, possible fragments of halogenated fullerenes, have been found in ICF extracts.[31,32] Furthermore, signals arising from fullerene oxides were observed in the ICF extracts. As the synthesis was carried out in the absence of any oxygen, we believe these fullerene oxides stem from highly reactive chlorinated fullerene species that hydrolyse during storage.

Because mass spectrometry only gives some qualitative indication of the abundance of the species present, HPLC analysis was performed to isolate individual fractions. Again, in comparison with EF extracts, for the ICF extracts "new" signals were observed with high intensities, some of which are similar to the intensity of C_{70}, especially in the range between the signals of C_{60} and C_{70} (Figure 3, graphs 3 and 4). Although the new signals observed eluting after C_{70} are smaller, they still have intensities higher than those of the signals of C_{76}, C_{78}, C_{82} and C_{84} in the EF soot. MS analysis of the indicated fractions in these regions (Figure 3, graphs 1 and 2) reveal several new fullerene cages not found in EF extracts. Although in general the typical eluting times for normal empty fullerenes are proportional to the size of the fullerene cage, that is, larger fullerenes elute later, there are many exceptions found for the ICF soots probably due to the varying number of chlorine atoms attached to the fullerene cages. Thus, several chlorinated species of C_{68} are found to elute between C_{70} and C_{84} (Figure 3). Correspondingly, the same fullerene cage sizes are observed at different elution times. This again is indicative of either the presence of different isomers, including non-IPR cages, and/or of the same fullerene species with different degrees of chlorination (numbers of attached chlorine atoms). Confirmation of the former or latter scenario can only be obtained after proper isolation and structural characterization of these compounds.

Optimization of the Synthesis Process

The experimental parameters applied during the explorative work in directly synthesizing halogenated fullerenes as described above were not optimized. Although the results were quite pleasing, we regarded it as beneficial to maximize the yields of chlorinated higher fullerenes. Before starting to vary the experimental conditions, we checked the robustness and reproducibility of the process employed so far by monitoring the evolution of the compounds formed during the process with time. For this purpose samples were removed after different intervals of time using the same CCl_4 flow rate of 0.2 mL/min. MS analyses showed that the same fullerene species are present in each sample harvested. Furthermore, the corresponding HPLC chromatograms are almost identical, which indicates that all extracts have the same composition. It can thus be concluded that the process is stable and the same species are formed in approximately the same relative amounts throughout the synthesis. Furthermore, three consecutive experiments using the same synthetic parameters showed no significant differences in product composition (MS/HPLC analysis), which indicates a good reproducibility of the synthesis process (for details see the Supporting Information).

Next the influence of CCl_4 concentration on product formation was investigated. Experiments were performed with rates of flow of CCl_4 (liquid) of 0.2, 0.3 and 0.4 mL/min. The toluene extracts obtained were analysed by LDI MS under the same conditions (Figure 4). The signals of C_{66}, C_{68}, C_{72} and C_{74} were chosen for further analysis because

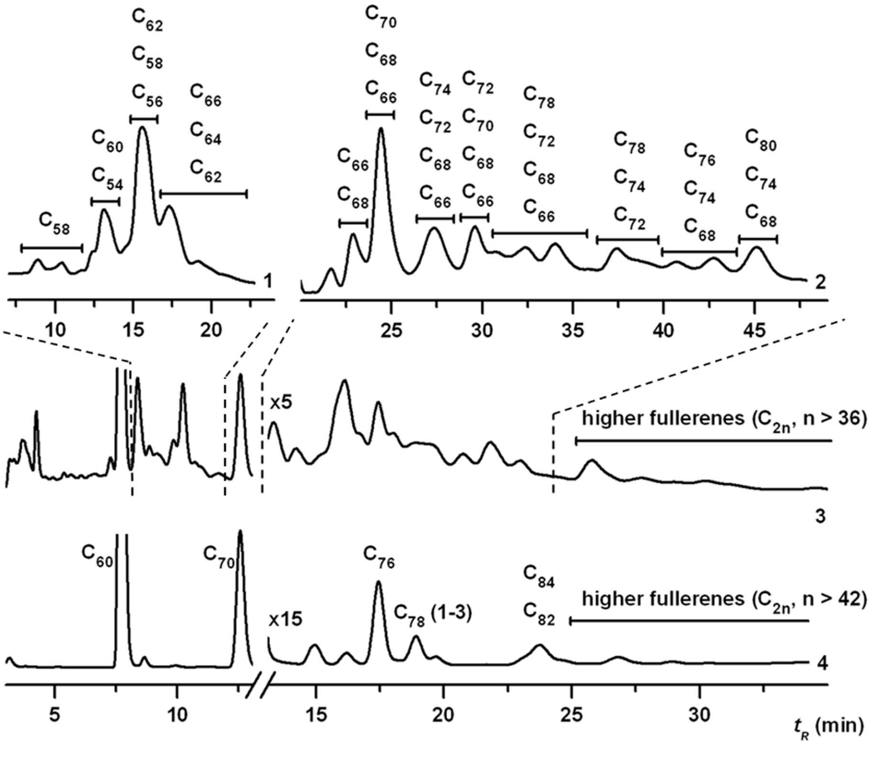

Figure 3. HPLC profiles for an empty fullerene extract (4) and a chlorinated fullerene extract (3) using toluene as eluent. For the sake of better resolution, the fractions between C_{60} and C_{70} (1) and after C_{70} until C_{80} (2) were analysed by using toluene/hexane (4:1) as eluent. The most abundant fullerene species are indicated above the corresponding retention maxima (MS analysis).

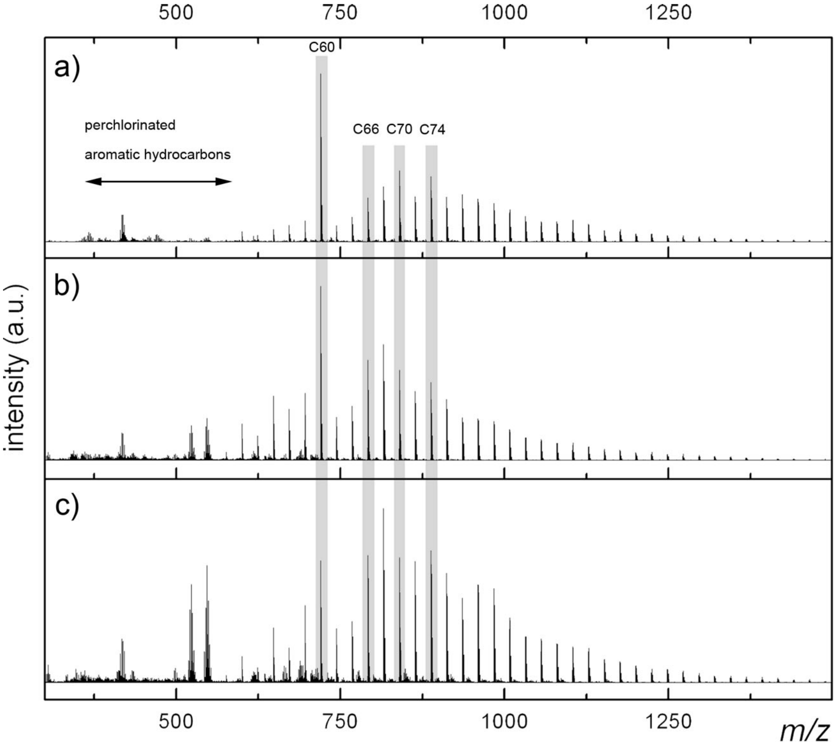

Figure 4. MS spectra (negative mode) of chlorinated fullerene extracts obtained at a flow rate of CCl_4 of a) 0.2, b) 0.3 and c) 0.4 mL/min.

their intensities reflect the abundance of the corresponding chlorinated fullerenes. It was found that increasing the concentration of CCl_4 results in a remarkable increase in the peak intensities of C_{66}, C_{68}, C_{72} and C_{74} relative to the peak intensity of C_{60}. At a flow rate of 0.4 mL/min the intensities of C_{66}, C_{68} and C_{74} exceeded even that of C_{60} (Figure 4). This indicates that the more chlorine that is present during the synthesis the more exohedrally chlorinated fullerenes can be obtained relative to pristine empty fullerenes. At the same time, an increase in the intensities of the signals corresponding to perchlorinated aromatic hydrocarbons is observed. This observation is also reflected by high background noise in the HPLC profile of the extracts from the experiment performed at a CCl_4 flow rate of 0.4 mL/min relative to the two other experiments with lower flow rates. Thus, although a higher CCl_4 flow leads to a higher relative yield of chlorinated fullerenes, the separation of these becomes significantly more difficult due to the growing fraction of perchlorinated aromatic hydrocarbons. Unless a protocol can be developed to separate the perchlorinated hydrocarbons from the chlorinated fullerenes before HPLC separation, the CCl_4 flow of 0.3 mL/min appears to be optimal for the production of chlorinated fullerenes.

Conclusions

We have shown that evaporating graphite in a HF furnace in the presence of CCl_4 leads to the direct production of halogenated fullerenes in high yields. This finding is of considerable importance because by this new route numerous unprecedented exotic carbon cage topologies have become accessible in high yields. Because attaching chlorine to C_n cages significantly relieves the strain of non-IPR systems as a result of a change from sp^2 to sp^3 hybridization, this approach appears to be generally suitable for the production of such non-IPR fullerenes and ultimately may also provide access to those finally free of chlorine. The most prominent new cage topologies encountered in this work, in addition to reported chlorinated cages like C_{50}, C_{54}, C_{56}, C_{64} and C_{66}, are C_{62}, C_{68}, C_{70}, C_{72}, C_{74}, C_{78} and C_{80}. It is important to emphasize that this method provides a particularly good access to chlorinated higher fullerenes. Our efforts are now being directed towards the separation of individual species for the complete characterization of their cage structure and number and patterns of attached chlorine atoms. So far we have isolated chlorinated C_{62}, C_{68} and C_{70}, two each of the C_{74} and C_{78} species and one C_{72} cage, which was found to be the non-IPR C_{2v}-$^{\#11188}C_{72}$ isomer in the form of $C_{72}Cl_4$ by single-crystal X-ray analysis.[33]

Experimental Section

General: The syntheses were carried out in a high-frequency induction furnace, the construction of which is as follows. Hollow cylinders of pure, isostatically pressed graphite (R6650, Kogo Kornmeyer Graphit Gmbh) serve as susceptors to heat up the reaction zone as well as carbon sources for the fullerene synthesis. The working coils are arranged around a water-cooled quartz tube extending above and below the graphite cylinder thus providing a homogeneous magnetic field (for more details see ref.[19]). Two heat shields surround the graphite susceptor to protect the external quartz tube and to insulate the reaction space around the graphite susceptor from heat loss. The outer shield is made of pyrolytic boron nitride, the inner one of carbon. The temperature can be monitored at the top of the inner side of the graphite body, where the temperature is highest, by using an optical pyrometer (Dr. G. Maurer GmbH TMRS 485-2-d Infrarot, Strahlungspyrometer). Carbon tetrachloride was used as chlorination agent. A HPLC pump (Sykam S1122) was integrated into the system to provide a constant and accurately adjustable flow of CCl_4 (see the Supporting Information for further details), which was kept constant during the experiments. Helium serves as the carrier gas at a flow rate of 2600 mL/min and the pressure during the synthesis was kept at 300 mbar. Water absorbed by the reactor walls was removed by evacuating the oven to 7×10^{-5} mbar for 1 h. Subsequently the graphite body was heated for 30 min to the evaporation temperature of around 2400 °C. The temperature was typically raised in seven distinct steps. The graphite starts to evaporate at around 2150 °C upwards to around 2400 °C. Injection of carbon tetrachloride was started directly after the final increase of temperature to the final synthesis temperature. Typical syntheses were carried out over a time of about 30 min. After the furnace generator was switched off, which abruptly stopped the carbon evaporation, the soot was collected (typically 300–400 mg) and soluble species were cold-extracted using toluene without any previous treatment. MS analysis was performed using a Shimadzu AXIMA resonance spectrometer in positive and negative modes. A Shimadzu HPLC system, equipped with a Buckyprep column (Cosmosil, Nacalai Tesque Inc., Kyoto, Japan), was used for quantitative analysis and separation of the chlorinated fullerene species in toluene solutions (UV/Vis detector, absorption detected at 290 nm unless stated otherwise).

Supporting Information (see also the footnote on the first page of this article): Scheme of the CCl_4 injection set-up, images of EF soot, images of ICF soot, MS spectra of different chlorinated fullerene species confirming the presence of attached chlorine atoms, HPLC chromatograms of the stability and reproducibility experiments, HPLC chromatograms and MS spectra for the experiments performed under different CCl_4 flow rates.

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