Synthesis of $C_{59}H_x$ and $C_{58}H_x$ Fullerenes Stabilized by Hydrogen

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Prolonged hydrogenation of C_{60} molecules by reaction with H_2 at elevated temperature and pressure results in fragmentation and collapse of the fullerene cage structure. However, fragments can be preserved by immediate termination of dangling bonds by hydrogen. Here we demonstrate that not only fullerene fragments but also hydrogenated fragmented fullerenes (e.g., $C_{58}H_{40}$ and $C_{59}H_{40}$) can be synthesized in bulk amount by high-temperature hydrogenation of C_{60}. We confirm successful synthesis of these species by matrix-assisted laser desorption ionization time-of-flight mass spectrometry and complete speciation of the resultant complex fullerene mixtures by high-resolution field desorption/ionization Fourier transform ion cyclotron resonance mass spectrometry.

Fullerene molecules that have lost one or more carbon atoms but have retained their cage structure are known as fragmented fullerenes.[1] These molecules are produced from C_{60} in the form of atomic clusters in gas phase and are typically observed only by mass spectrometry.[2,3] Isolation of fragmented fullerenes or their derivatives in bulk solid form is of a great interest for studies of their physical and chemical properties. Controlled fragmentation could also possibly lead to synthesis of small fullerenes, which are much less stable compared to C_{60} due to curvature stress effects. Also, small fullerenes must be much more chemically active due to presence of pentagon–pentagon junctions in the cage structure, which are absent in C_{60}. Stabilization by hydrogen and chlorine has been attempted for synthesis of C_{50} and C_{20} but they were isolated only in 1–2 mg amounts due to the complexity of the procedures.[4,5] Here we suggest that bulk synthesis of fragmented fullerenes can be achieved by gentle fragmentation of C_{60} by extreme hydrogenation. Prolonged hydrogenation results in fragmentation and collapse of the cage structure, but in contrast to other methods, the C_{60} fragments can be preserved due to immediate termination of dangling bonds by hydrogen.

A broad range of hydrofullerene molecules ($C_{60}H_{1-58}$) has been produced by reaction of C_{60} with H_2 at elevated temperature and pressure.[6-8] Prolonged hydrogenation results in fragmentation and collapse of the fullerene cage structure.[8] In a previous analysis of the products of prolonged C_{60} hydrogenation, matrix-assisted laser desorption/ionization time-of-flight

mass spectrometry (MALDI TOF MS) detected ions predominantly in the range, $730 < m/z < 750$. It was assumed that the observed peaks originate mostly from $C_{60}H_x$ molecules.[8] However, due to the limited resolving power and mass accuracy of MALDI TOF MS, the elemental composition of those species was not determined and $C_{60}H_x$ species could not be distinguished from $C_{59}H_{(x+12)}$ and $C_{58}H_{(x+24)}$ compounds of the same nominal mass. This limitation can be overcomed by use of high-resolution field desorption Fourier transform ion cyclotron resonance mass spectrometry (FD FT-ICR MS). Recently, C_{60} and complex petroleum mixtures have been successfully analyzed by FD FT-ICR MS.[9,10] Achieved mass accuracy (<1 ppm for broadband petroleum mass spectra, ∼200–1000 Da) allows unique elemental composition assignment. However, the FD FT-ICR MS experiment requires ion manipulation for prolonged intervals (up to a minute) compared to the millisecond time scale for MALDI TOF MS. As a consequence, gas-phase ion–ion and ion–neutral fragmentation can be more pronounced with FD FT-ICR MS.[9] Here, we employ both methods for analysis of the complex hydrofullerene mixtures.

Hydrogenation of pure C_{60} was performed at a pressure of 120 bar H_2 and temperature of 673 K with a typical material load of 0.5–1 g. One sample was hydrogenated with hydrogen flowing continuously for 1300 min (corresponding approximately to the weight maximum).[7] Two other samples were hydrogenated in a static hydrogen atmosphere for 1300 and 3000 min. MALDI analysis was performed with a reflectron TOF mass spectrometer (Biflex III, Bruker Daltonics, Billerica, MA). The hydrogenated fullerene samples were dissolved in toluene and mixed with dithranol matrix solution. FD FT-ICR MS experiments were performed with a home-built 9.4 T instrument.[10] Single 20–40 nL doses of saturated sample solutions (in toluene) were applied to the FD emitter.

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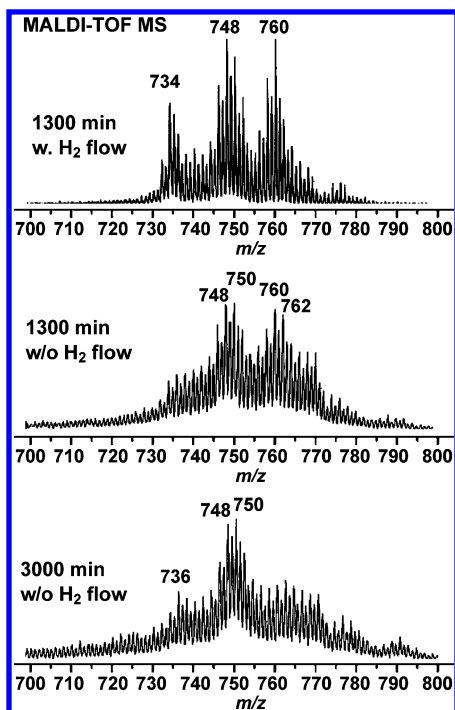[§] Rice University.
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Figure 1. MALDI TOF mass spectra of samples produced by hydrogenation of C_{60} at a pressure of 120 bar H_2 and temperature of 673 K with and without hydrogen flow.

MALDI TOF mass spectra for hydrogenated C_{60} samples are shown in Figure 1. The reference MALDI TOF mass spectrum of the $C_{60}H_x$ mixture produced by Benkeser reduction[11] demonstrated a ~20 Da wide peak distribution about a maximum at $m/z = 756$, corresponding to $C_{60}H_{36}$ (data not shown). The mass spectrum for the sample hydrogenated for 1300 min obtained with hydrogen flow (Figure 1, top) exhibits a broader distribution with maxima at $m/z = 734$, 748, and 760. Those maxima could be explained as the formation of $C_{60}H_{14}$, $C_{60}H_{28}$, and $C_{60}H_{40}$. However, presence of these species contradicts the high overall hydrogen content (~5 wt %), determined from elemental analysis and X-ray diffraction (more details on X-ray diffraction characterization of hydrogenated fullerenes have been published elsewhere[7,8]), corresponding to an average composition of ~$C_{60}H_{39}$. Furthermore, the distribution of peaks from this sample is much broader than from material obtained by chemical reduction and by reaction with H_2 gas performed under milder conditions.[6,12] Therefore, we propose here a different interpretation of MALDI TOF spectra. We suggest that $C_{60}H_{40}$ (760 Da) is the major product of the hydrogenation process, and that the molecule fragments during the synthesis by two mechanisms: loss of CH units with a termination of the dangling bond by hydrogen or loss of C_2H_2 units. The former results in formation of $C_{59}H_{40}$ (748 Da) and the latter produces $C_{58}H_{38}$ (734 Da).

The effect of prolonged heating is illustrated by MALDI TOF mass spectra obtained for the samples after 1300 and 3000 min static hydrogenation of C_{60} (Figure 1). The MALDI TOF mass spectrum of the 1300 min static hydrogenation sample shows prominent ions at $m/z = 760$ and 762 (possibly $C_{60}H_{40}$ and $C_{60}H_{42}$) as well as $m/z = 748$ and 750 (possibly $C_{59}H_{40}$ and $C_{59}H_{42}$), in agreement with the above interpretation. If the proposed model is valid, extension of the hydrogenation interval should result in complete fragmentation of $C_{60}H_{40}$ and $C_{60}H_{42}$ with a complementary increase in fragmentation. That trend is observed in the MALDI TOF mass spectrum for the 3000 min hydrogenation sample (Figure 1). This sample shows a strong
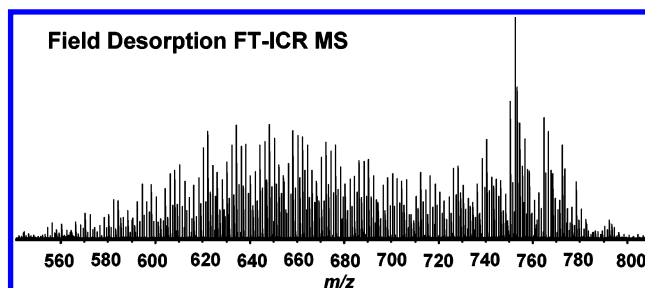

Figure 2. High-resolution FD FT-ICR mass spectrum of a C_{60} sample hydrogenated for 3000 min without hydrogen flow.
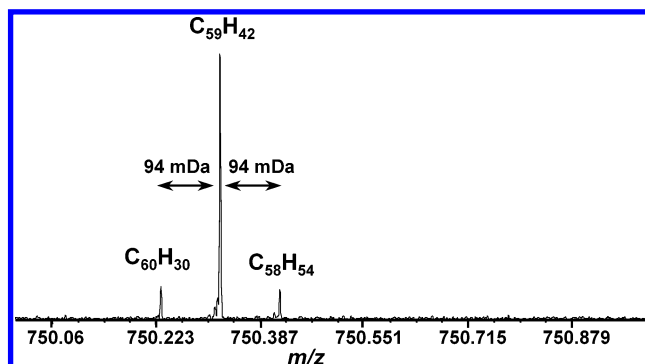

Figure 3. Expanded segment ($750 < m/z < 751$) of the FD FT-ICR mass spectrum of a hydrogenated fullerene sample (hydrogenated for 3000 min). The mass difference between neighboring monoisotopic peaks is ~94 mDa, corresponding to the mass difference between ^{12}C and $^1H_{12}$.
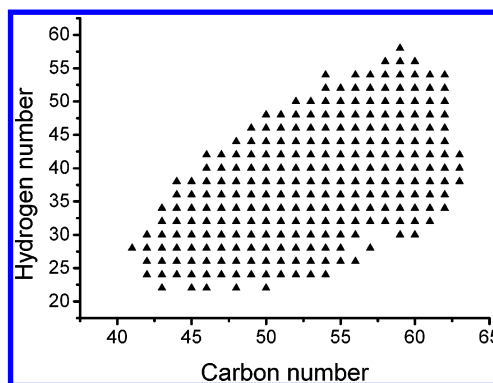

Figure 4. Elemental compositions of the components of the complex fullerene mixture shown in Figure 2.

reduction in magnitude at $m/z = 760$ and 762 (possibly $C_{60}H_{40}$ and $C_{60}H_{42}$) whereas ions of $m/z = 748$ and 750 (possibly $C_{59}H_{40}$ and $C_{59}H_{42}$) become dominant.

The presence of hydrogenated C_{59} and C_{58} is confirmed by high-resolution, high mass accuracy FD FT-ICR mass spectrometry. Compared to the MALDI TOF mass spectrum of the same sample, the FD FT-ICR mass spectrum for the 3000 minute static hydrogenation of C_{60} (Figure 2) exhibits higher relative abundance of lower mass species, attributed to ion–neutral and ion–ion reactions during the protracted ion manipulation events during FT-ICR mass analysis. Although it is not easy to estimate the extent of the gas-phase induced fragmentation, the advantage of high resolution and mass accuracy is manifested by the identification of the elemental composition of each ion in the mass spectrum (Figure 3). Mass peaks from hydrofullerenes of the same nominal molecular mass (for instance, $C_{60}H_{24}$ and $C_{59}H_{36}$), not resolved by TOF MS, are easily separated by FT-ICR MS (Figure 3).

As seen from Figure 4, a large number of fragmented hydrofullerene ions can be identified in the spectra. Their further

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reaction with CH (or C_2H_2) units lost during fragmentation resulted in formation of $C_{61}H_x$ and $C_{62}H_x$ molecules. It is very difficult to determine which of the fragmented hydrofullerene molecules were present in the sample after synthesis and which are a result of fragmentation during the FT-ICR MS experiment. Nevertheless, some very important chemical information about the sample composition can be extracted from Figure 4. It clearly shows that the minimum number of hydrogen atoms observed for all detected hydrofullerenes is ~21. The minimal hydrogen number for the most abundant species ($C_{60}H_x$, $C_{59}H_x$, and $C_{58}H_x$) is even higher: no such hydrofullerenes are observed with less than 28 hydrogens. Therefore, peaks in the MALDI TOF mass spectra below $m/z = 748$ ($m/z = 748$ could correspond to $C_{60}H_{28}$) in Figure 1 cannot be assigned to $C_{60}H_x$ molecules. Instead, they are likely to be hydrogenated C_{59} and C_{58} species. Therefore, the major species observed in the 3000 min hydrogenation sample are $C_{59}H_x$ and $C_{58}H_x$. The cage collapse of C_{60} upon very strong hydrogenation could possibly have been anticipated, based on the predicted reduced stability of highly hydrogenated fullerenes, but the appearance of fragmented fullerenes was unexpected.

In conclusion, prolonged hydrogenation of C_{60} molecules by reaction with H_2 gas at elevated temperature and pressure results in formation of hydrogenated fragmented fullerenes (e.g., $C_{58}H_{40}$ and $C_{59}H_{40}$), which can be synthesized in bulk amounts. Hydrogenation conditions (temperature, pressure and reaction period) can be modified widely to enable synthesis of a variety of products. With these methods, fullerenes may now be used as raw material for the bulk production of smaller fullerenes by controlled fragmentation.

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