Building Carbon Bridges on and between Fullerenes in Helium Nanodroplets

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Supporting Information

ABSTRACT: We report the observation of sequential encounters of fullerenes with C atoms in an extremely cold environment. Experiments were performed with helium droplets at 0.37 K doped with C60 molecules and C atoms derived from a novel, pure source of C atoms. Very high-resolution mass spectra revealed the formation of carbenes of the type C60(C)n, with n up to 6. Bridge-type bonding of the C adatoms to form the known dumbbell C60≡C≡C60 also was observed. Density functional theory calculations were performed that elucidated the carbene character of the C60(C)n species and their structures. Mass spectra taken in the presence of water impurities and in separate experiments with added H2 also revealed the formation of the adducts C60Cn(H2O)n and C60C2(H2), probably by H−OH and H−H bond insertion, respectively, and nonreactivity for the dumbbell. So C adatoms that form carbenes C60(C)n can endow pristine C60 with a higher chemical reactivity.

Since the discovery of fullerene in vaporized graphite and its assignment by Kroto et al. and confirmation by Krätschmer et al., the growth mechanisms of fullerene formation under energetic conditions have been a matter of debate. Simultaneously, several routes to add functional parts to fullerenes have been highly successful, including cyclopropanation, Diels−Alder reactions, and carbene additions. Derivatized fullerenes have promising applications in material and life sciences. They are used as electron acceptor molecules in solution-processed organic photovoltaic cells, they are considered for biological and medical applications, for DNA manipulation, and for biosensors, and they have been successfully deposited on surfaces as novel self-assembled monolayers. The possibility of activating reactive fullerenes with C atoms to form carbenes that can promote subsequent fullerene derivatization has driven us to investigate these species more closely. We performed laboratory experiments designed to explore encounters of fullerenes with C atoms derived from a clean source of C atoms. Such encounters may also occur in natural environments such as interstellar space where C60 and C60 have been detected. Quite recent experiments under energetic conditions with laser-ablated carbon vapor and C60 under a flow of helium suggest that the carbon vapor can promote C exchange, C60 isomerization, and C atom incorporation, leading to fullerene closed network growth under these conditions. Also, under the hot conditions in fullerene plasma experiments, Shvartsburg et al. proposed the existence of ball-and-chain type fullerene dimers connected with one or more C atoms.

C additions to C60 were also predicted to catalyze Stone−Wales transformations.

There has been a recent breakthrough in pure C atom production. Low-energy carbon atoms now can be produced with a purity >99% from a thin-walled, sealed tantalum tube containing carbon. We have adopted this source to investigate the reactivity of C60 toward C atoms in very low-temperature He droplets and modified our apparatus that allows C60 molecules to be added into He droplets (ca. 106 He atoms and five C60 molecules on average per droplet) where they can aggregate and be cooled to the droplet temperature of 0.37 K. Carbon atoms are then added and allowed to react with the C60 aggregates before the droplets are exposed to ionizing or attaching electrons that permit reactants and products to be analyzed with a mass spectrometer. While low-energy (<22 eV) electrons can attach directly, higher energy electrons (>22 eV) first generate either He+ or He2+ that then ionizes neutrals inside the droplet.

To vary the C input into the droplet, the electric power used to heat the tantalum tube was varied from ca. 60 to 162 W.

Mass spectra recorded for adduct formation with up to six carbon atoms to C60 are shown in Figure 1. The two stable isotopes of carbon, 12C (98.93%) and 13C (1.07%), lead to a characteristic series of mass peaks when combined with

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products are subsequently ionized. The structures of the isotopologue $^{12}$C$_{55}$ is almost the same, and thus the latter case the C$_{60}$ cage distorts more. The typical bond length of the [6,6] bond, where C is adsorbed, is 1.582 Å for the [6,6] bond and that of the distributed single adatom structure for C$_{64}$ is 2.018 Å.

Remarkably, the observed mass distribution is quite similar for positive and negative ions despite the substantial differences in the mode of ionization. Positively charged ions are predominantly formed via charge transfer from an initially formed He$^+$ ion, which approaches the C$_{60}$C$^-$ via resonant hole-hopping, whereas the dominant process for anion formation at 22 eV is due to He$^{*-}$, which is resonantly formed at this electron energy and attracted by the polarizable C$_{60}$C$^-$.

Figure 1. Mass spectra recorded for C$_{60}$C$^+$ (bottom) and C$_{60}$C$^{-}$ ions (top) for He droplets (nozzle temperature 9.5 and 9.7 K, respectively) containing C$_{60}$ and $^{13}$C atoms. The ionizing energies are 70 and 22 eV, the C$_{60}$ oven temperatures were 292 and 288 °C, and the power settings for the $^{13}$C source were 158 and 162 W, respectively. Note the presence of water impurities. (See the text.) The inset shows enlarged features that two carbon atoms adsorb next to each other at the same hexagonal or pentagonal face. The adatoms should be immobile once they are adsorbed at these low temperatures.

Computations indicate that a single carbon adatom chemically binds to the C$_{60}$ cage at both distinguishable bond positions, that is, between two hexagonal faces [6,6] with 3.09 eV or one hexagonal and a pentagonal face [6,5] with 2.83 eV. Later density functional theory (DFT) calculations identified the [6,5] bridge as the most stable favored by 0.3 eV. Our own DFT calculations with results summarized in Table 1 in the Supporting Information agree with this latter stability order; we found that the [6,6] bond is slightly preferred to the [6,5] bond with a bond energy $D_e$ (dissociation energy of the carbon adatom) of 2.82 eV on the [6,5] bond. This compares with 3.52 eV for the cation and 3.39 eV for the anion. C$_{60}$C also was seen to have carbene properties from a natural bond orbital analysis. The resulting doubly occupied lone-pair orbital of the 61st carbon atom in singlet C$_{61}$ is shown in Figure 2a. Further calculations provided an ionization energy of 6.37 eV for C$_{61}$, significantly smaller than 7.08 eV for C$_{60}$ and an electron affinity of 2.43 eV, larger than 2.25 eV for C$_{60}$ and a fairly large dipole moment of 1.27eD (with $\mu_1 = 1.1855$ D, $\mu_2 = 0.0000$ D, and $\mu_3 = 0.4735$ D).

In the case of two carbon adatoms, the reference structure is shown in Figure 2b with two [6,6] C adatoms that are situated normal to each other with respect to the fullerene center. The adatoms can also adsorb very close to each other on neighboring bonds of a single carbon hexagon (Figure 2c); this structure is only 0.013 eV less stable than the reference structure, an amount that is not significant for DFT. We also considered other structures. A high-energy gain of 3.97 eV compared with the structure shown in Figure 2b can be reached by adsorbing the two carbon atoms in a bent chain on a [6,6] position, as shown in Figure 2d. Adsorption of two carbon atoms at opposite bonds of a pentagon face leads without barrier to a very stable (−5.3 eV) C$_{60}$ cage structure with two heptagons and a tetragon (almost square, Figure 2e). In this noncarbene cage all carbon atoms are bound to three neighbors, and lone pairs are absent in the natural bond orbital analysis.

For C$_{63}$ (C$_{64}$) we find that adsorption of a C−C−C (C−C−C) chain on a [6,6] position is energetically favorable by −7.13 eV (−10.83 eV) compared with distributed single adatoms. The C−C−C structure for C$_{65}$ is shown in Figure 2f and that of the distributed single adatom structure for C$_{64}$ is shown in Figure 2g. The perfectly symmetric structure for C$_{66}$ with six single carbon adatoms at [6,6] positions (Figure 2h) is energetically unfavorable by only 0.038 eV compared with 6 C adatoms at [6,5] positions, as shown in Figure 2i. We did not calculate chain structures for more than four adatoms. Adding an additional C atom to the perfectly symmetric C$_{66}$ gives C$_{67}$. The dissociation energies for distributed adatoms from C$_{61}$ to C$_{67}$ lie in a range of 2.49 to 2.82 eV for one to six carbons. For seven adatoms the dissociation energy decreases to 1.94 eV. In the latter case the C$_{60}$ cage distorts more. The typical bond length of the [6,6] bond, where C is adsorbed, is 1.582 Å for C$_{64}$. For two of the seven C adatoms in C$_{67}$ this bond length is stretched to 1.618 Å.

In summary, the computations predict the existence of a variety of different stable isomers for which fullerene cage growth is energetically favorable compared with C−C−... chain attachment, which is, in turn, favorable to the well-separated addition of up to at least seven single C atoms. The
well-separated addition is proposed to occur in our experiments in a cold environment due to rapid cooling accompanied by trapping in local minima on the potential energy surface, whereas cage growth is likely favored at higher temperatures as in the experiments of Dunk et al. The carbene character of bridge-type C\(_{60}(C)\) is clearly manifested by the natural bond orbital analysis that is displayed in Figure 2a for C\(_{60}(C)\). Carbone character can be inferred for all experimentally observed C adducts C\(_{60}(C)\) from the observed water impurity adduct C\(_{60}C\)\(_n\)(H\(_2\)O)\(_n\)\(\pm\) ion peaks in Figure 1. According to the presence of these peaks, C\(_{60}(C)\) molecules with \(n > 0\) pick up H\(_2\)O, as would be expected from a carbene reaction, presumably by H–OH bond insertion, while C\(_{60}\) itself adds H\(_2\)O only by physisorption. Furthermore, the results of our separate experiments with added H\(_2\) dopant (see Figure 3 and Figures 1S and 3S in the Supporting Information) indicate H\(_2\) additions for each C\(_{60}(C)\) with \(n = 1,2,3,4,5\), presumably by H–H bond insertion. These results with H\(_2\)O and H\(_2\) strongly indicate sequential surface addition of at least the first five carbon atoms to form carbenes of the type C\(_{60}(C)\) with \(n = 1–5\) instead of energetically favorable C chains such as C\(_{60}C=CC=CC\), for which always only one H\(_2\)O or H\(_2\) would add chemically (H\(_2\) at \(T = 0.37\) K does not add chemically to C\(_{60}\) because of a large barrier predicted to be 1.69 eV). This result shows that C-atom additions can transform a chemically inert (against reaction with H\(_2\) and H\(_2\)O) fullerene C\(_{60}\) into chemically reactive carbenes C\(_{60}(C)\). Carbenes are known from terrestrial chemistry to be among the most versatile and synthetically useful reactive intermediates. Carbine additions to fullerenes have already attracted considerable attention.

Figure 2. (a) Lone pair orbital at the C-adatom in singlet C\(_{60}\) [6,5] from a natural bond orbital analysis. Structures computed with DFT calculations for C\(_{62}\) (b–e), C\(_{63}\) (f), C\(_{64}\) (g), and C\(_{66}\) (h, i).

Figure 3. Mass spectra recorded for \(^{12}\)C\(_{60}\)\(^{13}\)C\(_n\)H\(_{2n}\)\(^+\) ions for droplets containing C\(_{60}\)\(^{13}\)C\(_n\) and H\(_2\). The ionizing energy is 70 eV, the C\(_{60}\) oven temperature is 292 °C, the power setting for the \(^{13}\)C source was 162 W. The ambient pressure of H\(_2\) was 0.5 mPa.
Carbenes should also play a similar role in interstellar chemistry.37 Our experiments demonstrate the reactivity of C60(C:)m toward H2 and H2O. We expect similar reactivities toward many other molecules as well as other carbenes such as :CO, :CS, :C2+, :C3, O, and :CNH, for example.37 Our other recorded mass spectra show evidence of the presence of C adduct ions for clusters of fullerenes of the type (C60)2/(C60)2C with m = 1 to 9 and n = 1–5 including the dumbbell. Excerpts are shown in Figure 4 for (C60)2/0(C)x with m = 0–3. The positive and negative ion spectra both show a remarkable predominance of ionized (C60)2C suggesting the occurrence of neutral chemistry before ionization and a special stability for neutral (C60)2C, presumably the dumbbell C60. The concomitant observation of the dication appears to be stable against Coulomb explosion; presumably the two charges are located apart on the two fullerene molecules such as C60(CH(H))n, C60(CH(OH))m, C60(C=CO)n, and even C60(C=C60) wśród C60.40

Photochemical and photophysical properties of the three bridged isomers [6,6]–[6,6], [5,6]–[6,6], and [5,6]–[5,6] also have been reported.31,42 Under energetic conditions C and C2 addition to fullerenes leads to closed network growth as demonstrated by Kroto et al.5,22 whereas our observed surface C additions at low temperature enhance the chemical activity of the surface of C60 by carbene formation. The latter may pave the way toward a generation of a new class of fullerene derivatives. Reactive C60 carbene species may also be formed in interstellar and circumstellar environments containing C and C60, where they could add H2 and H2O, as well as C60, to form derivatized fullerene molecules such as C60(CH(H))n, C60(CH(OH))m, C60(C=CO)n, and even C60(C=C60) wśród C60.40

Figure 4. Upper part: Mass spectra recorded for C60C(C60/0(C)x ions (left) and C60Cn(C60/0(C)x ions (right) for He droplets (nozzle temperature 9.5 and 9.6 K, respectively) containing C60 and 13C atoms. The ionizing energies are 90 and 22 eV, the C60 oven temperatures were 308 and 300 °C, and the power settings for the 13C source were 141 and 150 W, respectively. Note the presence of water impurities (see text). Lower part: Mass spectra recorded for (C60)2/0(C)x ions for droplets containing C60/0(C)x and H2. The ionizing energy is 70 eV, the C60 oven temperatures are 292 °C, and the power setting for the 13C source was 162 W. The ambient pressure of H2 was 0.5 mPa.

EXPERIMENTAL SECTION

He droplets were formed by expanding helium (Messer purity 99.999%) from a stagnation pressure of 2.4 MPa through a 5 μm nozzle, cooled by a closed-cycle refrigerator (Sumitomo Heavy Industries LTD, model RDK-415D) to ~9.5 K, into vacuum. The average size of the He droplets is ~106 atoms.43 The resulting supersonic beam was skimmed by a 0.8 mm conical skimmer located 1 cm downstream from the nozzle and flew through two 10 cm long, differentially pumped pick-up regions. Small amounts of C60 (MER, purity 99.9%) were vaporized at an oven temperature between 292 and 308 °C and picked up by the He droplets with almost unity efficiency upon collisions. In the second differentially pumped pickup chamber atomic (purity >99%) vapor of 13C emitted from a heated sealed tantalum tube containing carbon is picked up by the He droplets.19 H2 (Messer, purity 99.999%) was introduced via an electronically controlled leak valve into the first pickup chamber. Water was present in the machine as a trace impurity from the residual gas. The doped helium droplets were ionized by collisions with electrons at energies ranging from 0 to 100 eV. The ions were accelerated to 40 eV into the extraction region of a commercial orthogonal time-of-flight mass spectrometer equipped with a reflector (Tofwerk AG, model HTOF). For anions the mass resolution was m/Δm ≈ 2500 and for cations 3500. The base pressure in the mass spectrometer was 10−9 Pa. The ions were detected by a microchannel plate and recorded via a time to digital converter. Additional experimental details have been described elsewhere.44 Special home-built software was utilized to deduce ion intensities from the mass spectra, taking into account all possible isotopologues, as shown in Figure 2S in the Supporting Information.5

Energetics and geometries of neutral C60 with carbon adatoms were calculated by means of DFT. All structures were fully optimized to account for deformations of the fullerene due to the presence of the carbon adatoms. We used the B3LYP46,47 hybrid density functional and a standard 6-31g(d)48 basis set as implemented in the Gaussian 09 program.49 Energies were corrected for zero-point vibrations, and all reported structures are true local minima. The accuracy of isomerization energies and heats of formation of B3LYP with the 6-31g(d) basis set was estimated with 0.13 eV for a large set of neutral, closed-shell organic compounds containing C, H, N, and O.50
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