Density of fullerene containing soot as determined by helium pycnometry

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Mass-spectrometric techniques have demonstrated the presence of carbon clusters C_{2n} with n as high as 300, in carbon soot material produced using the "arc-synthesis" method. While new techniques are being explored for solvation of larger fullerene cages, beyond the more conventional solvation of the "smaller" fullerene molecules such as C_{60} and C_{70}, the question arises: how much of the soot is fullerene cage molecules? One expects the density of fullerene soot composed of, say, C_{240} and larger cages, to be significantly less than graphite, 2.2670 g cm^{-3}, and also less than C_{60}, 1.65 g cm^{-3}. The helium pycnometry determined density of a sample of commercially available raw "fullerene" soot is 1.5651 g cm^{-3}. It is likely that this is an upper bound to the density, due to permeation by helium resulting from the large size of some fullerenes present in the soot.

1. Introduction

The question of the chemical makeup of raw soot as produced by carbon arc with about 100 Torr of helium [1,2] is still an open one. There is little doubt that fullerene cages substantially larger than C_{60} are present, based on mass-spectrometric analysis of such soot [#1]. The diameter of one possible structure [6] for C_{540} is stated to be about three times the diameter of C_{60}. If we take the diameter of C_{540} as 30 Å and assume a spherical shape and a fcc closest-packed crystal structure, simple scaling of the known density of C_{60}, 1.65 g cm^{-3}, yields a density of about 0.55 g cm^{-3}. Perhaps a better estimate is obtained by scaling the nuclear framework diameter of C_{60}, and adding the van der Waals diameter of C to the nuclear framework. This is done by calculation of the number of C's per unit surface area for C_{60}, with the radius of the sphere 3.55 Å. if we assume the same number of C's per unit area for larger (hypothetical) spherical fullerenes, a C_{540} nuclear framework diameter of 10.65 Å is determined. Addition of a C-atom van der Waals diameter of 3.0 Å yields a fcc crystal density for this hypothetical C_{540} fcc crystal of 1.03 g cm^{-3}.

Smaller fullerene molecules such as C_{60} and C_{70}, C_{76}, C_{78}, C_{84} are presently extracted with toluene or benzene [1,7,8]. Extraction of larger fullerenes is more difficult because of their much larger binding energy in the carbon matrix (soot). The pair potential well depth of C_{60} dimer is about 7 kcal/mol [9]. The van der Waals binding of C_{540} to surrounding fullerene molecules could be several hundred kcal/mol, or higher (for footnote 2 see next page). Use of higher boiling point solvents as well as ultrasonic agitation has allowed extraction of C_{2n} molecules up to about C_{300} (for footnote 3 see next page), [10] but the material extracted with these new methods represented only 15 wt% of the soot left after extraction with toluene [10]. The question arises: What does the rest of the carbon soot consist of?

The density of carbon soot is one useful indicator of the fullerene content, and where the fullerene mass distribution is peaked. For example, it is possible to run the arc synthesis method so that the mass-spectrometric-measured fullerene distribution is skewed away from C_{60} [11], or towards C_{60}, as is presently being done by most research groups. The mass-spectrometric techniques as employed on raw soot do not determine the fullerene concentrations. They probe, to some extent, whether molecules of formula C_{2n} are present.

The fullerene soot material is a multicomponent mixture. Helium pycnometry measures the true density for perfect crystals if the helium does not diffuse into the crystal. It is, however, likely that helium would diffuse into a perfect crystal of a particular isomer of C_{540} because the spacing between closest-packed C_{540} molecules would allow it. For this reason we expect helium pycnometry to provide an upper bound to the density of the raw soot powder, and as such it is a useful experimental technique to indicate fullerene content. the low density determined, see below, is therefore suggestive of high fullerene content, but does not allow quantitative determination of the fullerene distribution in the powder.

2. Experimental

The densities of three different samples were determined with the Micromeritics AccuPyc 1330 instrument with a 10 cm^3 capacity. The three samples were: C_{60} containing soot produced in about 100 Torr of helium (Texas Fullerenes); graphite rod (Poco Graphite); the same graphite rod, but ground to a powder.

The C_{60} rich soot was pelletized in a 12.7 mm diameter press, with about 0.1 g of soot added and then compressed to 4000 psig, another 0.1 g added and compressed, and so on until a pellet weighing 0.5675 g was obtained. The pycnometer was programmed to perform 20 purges, followed by analysis using the run precision option set at 0.03% of full scale capacity (10 cm^3). Both purge and analysis fill pressures were set at 19.5 psig, and an equilibration rate of 0.005 psig/min was used.

Two sections of the graphite rod were weighed (3.7103 g total) and their density determined in exactly the same way as that described above. 4.5294 g of graphite powder was made from the same rod with an ultrasonically cleaned stainless steel file, and the density determined as described above.

3. Results and discussion

The graphite rod density was determined to be 2.0372 g cm^{-3}; the graphite powder density 2.1445 g cm^{-3}; and the pelletized C_{60} containing soot 1.5641 g cm^{-3}.

The graphite rod (powder) densities were determined as a check on the experimental method. The 0.1073 g cm^{-3} difference in densities is due to the presence of excluded volume pores in the graphite rod which are present because the rods have relatively high porosity. For comparison, the density of perfect single-crystal graphite is 2.2670 g cm^{-3} [12].

The density measurement for the fullerene soot represents, as discussed above, an upper bound to the true density. A true density could be defined as represented by each component of the multicomponent mixture present as a perfect single-crystal, with appropriate summation to give the average density. Of course the carbon soot powder is not so ideally configured! Helium pycnometry of this carbon soot cannot tell us what the true average density is, as defined above, but the very low 1.56 g cm^{-3} determined is suggestive of the presence of large quantities of carbon cage molecules, and very little graphite powder. It is hoped that this number will serve as further impetus to extract and separate the larger carbon cage molecules present in the C_{60}-rich soot.

[#1] Laser ablation, FT-ICR technique [3]. Ar ion sputtering with TOF-MS technique [4]. Laser desorption of raw soot, FT-ICR technique [5].

[#2] R.S. Ruoff: assume a spherical C_{540} with diameter 30 Å. The surface area is therefore 2827 Å^2. The projected area of C_{60} is 78.5 Å^2, and closest packing of circles on a flat 2D surface allows 91% coverage. Therefore a lower bound of roughly 30 C_{60} molecules could closest pack around the hypothetical C_{540} molecule. A better estimate is obtained by actual model building: precision metal spheres with a diameter ratio of 3:1 and some super glue were used to show that 50 of the smaller spheres could be attached to the larger sphere. Preliminary calculations (with T. Jackman) yield a binding energy between C_{60} and graphite of about 20 kcal/mol. With this binding energy as an approximate value for C_{60} on C_{540}, the binding energy of the C_{540} with the 50 surrounding C_{60} molecules is 1000 kcal/mol C_{540}, which is indeed a very large binding energy!

[#3] See "Note added in proof" in ref. [8].

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4. Conclusion

Helium pycnometry has been used to provide an upper bound for the density of a typical sample of C_{60} containing carbon-soot powder. The low number measured, 1.565 g cm^{-3}, indicates the presence of a large quantity of carbon cage molecules.

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Formation of endohedral carbon-cluster noble-gas compounds with high-energy bimolecular reactions: $C_{60}He^{n+}$ $(n=1, 2)$

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Results are reported for high-energy beam studies of the formation of adduct ions in the reactions of $C_{60}^{+\cdot}$ and C_{60}^{2+} with He and D_2 in a four-sector mass spectrometer. Studies of the addition of He to $C_{60}^{+\cdot}$ at translational energies of 2, 3, 4, 5, 6 and 8 keV showed optimal adduct formation from 5 to 6 keV. The $C_{60}He^{2+}$ adduct was observed in collions between C_{60}^{2+} and He at 6 keV translational energy. No adduct formation was observed between D_2 and $C_{60}^{+\cdot}$ or C_{60}^{2+} at 6 keV translational energy.

1. Introduction

The impact that the production and availability of fullerene molecules has had on chemistry is common knowledge [1]. One new field of chemistry which has been spawned is that of endohedral chemistry – chemistry proceeding inside a cage of (carbon) atoms [2]. A case has been made by Smalley et al., although opinions differ [3], that the metal-containing cluster ions $C_{60}M^+$ (with M=La, Ni, Na, K, Rb, and Cs) which have been observed in the mass spectra of the laser-induced vapors of graphite doped with metal salts are spherical C_{60} molecular ions with the metal atom located inside. Mass-spectrometric experiments in our laboratory have shown that He may be injected into singly [4], doubly [5], and triply [5] charged C_{60} cations, but only the observed fragmentations have been reported [#1]. Shortly thereafter Ross and Callahan [6] were able to identify $C_{60}He^{+\cdot}$ unambiguously and to show that the helium adduct formation in the high-energy collision of $C_{60}^{+\cdot}$ with He is not necessarily accompanied by expulsion of a neutral fragment [#2]. In the meantime, we have learned from extensive $C_{60}^{+\cdot}$ collision experiments at various kinetic energies and with several different scan modes that the cross section for He attachment is strongly dependent on energy and that the linked-scan mode used in our initial experiments for fundamental reasons was not ideal for the unambiguous detection of $C_{60}He^{+\cdot}$. We report here a confirmation of the direct formation of $C_{60}He^{+\cdot}$ from the collision of $C_{60}^{+\cdot}$ with He reported by Ross and Callahan, the dependence of the efficiency of the formation of this adduct on kinetic energy, the failure of D_2 to add with a measurable efficiency to $C_{60}^{+\cdot}$ and C_{60}^{2+}, and the first observation of the direct formation of the adduct ion $C_{60}He^{2+}$ from the collision of C_{60}^{2+} with He.

2. Experimental

The experiments were performed with a four-sec-

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[#1] The incorporation of Ne was also observed, but only for singly-charged $C_{60}^{+\cdot}$ cations, and with a much smaller efficiency [4]. Furthermore, $C_{60}He^{+\cdot}$ was observed in the fragmentation spectrum produced by the collisions of 8 keV $C_{70}^{+\cdot}$ ions with He [4].

[#2] Although we also saw signals in our mass-spectrometer experiments performed at 8 keV kinetic energy that could explain the formation of $C_{60}He^{+\cdot}$, we did not report these in our initial communication [4].

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