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Characterization of C_{60} and C_{70} Clusters

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Abstract: C_{60} and C_{70}, new molecular forms of carbon, have been produced in macroscopic quantities and characterized by thermal desorption mass spectrometry, IR absorption, UV absorption, NMR, ESR, high performance liquid chromatography, electrochemistry, and transmission electron microscopy. Individual C_{60} molecules have been detected by transmission electron microscopy. Electrochemistry studies show that at least three anionic forms of C_{60} (C_{60}^{1-}, C_{60}^{2-}, and C_{60}^{3-}) and C_{70} can be produced in solution. Electron spin resonance studies of C_{60} show no evidence for any free spin. Purified samples of C_{60} and C_{70} are obtained by liquid chromatography. High-performance liquid chromatography (HPLC) shows that the retention time for C_{60} is smaller to that for 4-ring aromatic hydrocarbons. Chemical ionization mass spectrometry (CI-MS) shows that electron capture is more favorable than protonation for C_{60} and C_{70}. IR spectra of chromatographic separated C_{60} and C_{70} are contrasted.

Introduction

A technique for preparing and isolating macroscopic quantities of C_{60}, "a new form of carbon", recently reported by Krätschmer and co-workers,[1,2] has opened the way for probing the properties of C_{60} and related molecules. Our work, as well as that from several other groups,[3-9] now confirms that C_{60} (and C_{70}) can be synthesized in large quantities. In their original work, Krätschmer et al. characterized the new C_{60} material by mass spectrometry, IR and UV-vis absorption spectroscopy, and X-ray and electron diffraction.

In this paper we extended the characterization of C_{60} and C_{70} using a variety of experimental probes. Our NMR and UV-visible spectra of C_{60} and C_{70} are consistent with those recently reported by others.[3-5] We have characterized the molecules using thermal desorption mass spectrometry with both electron impact ionization and chemical ionization detection, IR absorption, ESR, high-performance liquid chromatography (HPLC), electrochemistry, and transmission electron microscopy. Simultaneous positive and negative ion detection with chemical ionization mass spectrometry (CI-MS) shows that electron capture is significantly more favorable than protonation for both C_{60} and C_{70}. IR absorption spectra of purified samples of C_{60} and C_{70} reveal both closely overlapping, and distinctive, isolated absorptions for the two species. Electrochemical studies detect at least three and possibly four anionic forms of C_{60}, and three anionic forms of C_{70}. ESR studies show no evidence for any free spins for C_{60}. HPLC studies allow quantitative measures of the mass fractions and show that the C_{60} retention time is similar to that for smaller 4-ring aromatic hydrocarbons such as $C_{18}H_{14}$. Isolated C_{60} (C_{70}) molecules are observed on MgO crystals by TEM.

Synthesis and Extraction of C_{60}

Our production technique is similar to that outlined in ref 9 in which two carbon electrodes kept in loose contact are resistively heated in a chamber containing about 100–200 Torr of inert gas (argon in our case). The exact conditions used to establish the smoking conditions from which 1 to 10% C_{60} can be extracted from the deposited carbon "soot" primarily depend on several parameters including (a) the rod size, (b) the contact pressure of the two rods, or if arcing conditions are established, the separation between the two electrodes, (c) the rare gas pressure, and (d) the electrical current through the rod. The carbon smoke is deposited on the surrounding glass and metal surfaces from which it is collected.

C_{60} (as well as C_{70} and possibly other C_{2n}) is extracted from these deposits since it dissolves in many solvents, e.g. benzene, toluene, cyclohexane, carbon tetrachloride etc. We simply extracted the toluene soluble material. After evaporation of the toluene, the solid residue was then examined by mass spectrometry and IR spectroscopy confirming that C_{60} and C_{70} were by far the dominant pure carbon species present in the sample. In addition, both thermal desorption mass spectrometry and IR absorption spectroscopy identified that hydrocarbons were also present. Diethyl ether selectively extracts these hydrocarbons, as suggested by Krätschmer et al.,[1] leaving behind a solid material consisting almost entirely of C_{60} and C_{70} as confirmed by mass spectrometry and NMR. Subsequently, purified samples of separated C_{60} and C_{70} are obtained by chromatographic separation.

Characterization of C_{60} and C_{70}

A. Mass Spectrometry. The presence of C_{60}, C_{70}, and other C_n ($n > 40$) was first discovered by mass spectrometry (MS) in studies of gas-phase carbon clusters.[10] Subsequently conditions were found under which C_{60} could be made to be the dominant ion in a time-of-flight mass spectrum ($n < 100$) with C_{70} the next most intense peak.[11] The presence of C_{60} and C_{70} in the carbon "soot" is easily confirmed by MS.[1,5] A small amount of the solid C_{60}/C_{70} material left after solvent extraction (see above) is loaded into a direct insertion probe which is inserted into the ion source of a Finnigan TSQ-46 mass spectrometer.[12]

1. Electron Impact Ionization. Mass spectra are continuously acquired from m/z 300 to 875 at 2 s per scan as the probe temperature increased up to ca. 400 °C. Figure 1 shows the evolution of the m/z (mass-to-charge) 720 and 840 ions as a function of probe temperature when a 70-eV electron beam is used for ionization. As can be seen, the signal for C_{60} starts at about 300 °C whereas the initial signal for C_{70} begins at about 350 °C, and, in fact, these are the only two species present in measurable quantity which desorb between 250 and 400 °C.[13] This supports the observation by Krätschmer that C_{60} (and C_{70}) can be separated from the carbon "soot" by sublimation at about 400 °C and also suggests that the fullerenes may have different desorption energies and thus may be separated from each other by carefully controlling the sublimation conditions.

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(12) The mass spectral patterns obtained from a quadrupole mass spectrometer strongly depend on the tuning of the instrument. Our tuning was set for characterizing heavy organic ions. With use of a calibration compound, perfluorobutylamine (FC43), the intensity of the m/z 219 ion was set to be slightly greater than that of the m/z 69 ion. The intensities of the m/z 502 and 614 ions are about 20% and 4% of that of the m/z 219 ion.

(13) Below 200 °C a large number of low mass peaks are detected when a non-ether washed sample is used. These peaks have all disappeared by about 200 °C.

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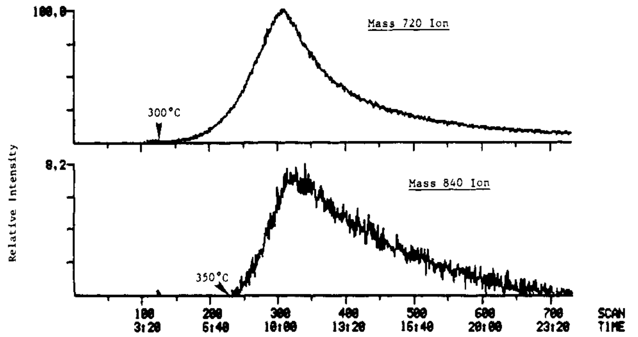

Figure 1. The temperature profiles of the sublimation of C_{60} and C_{70} under mass spectrometric vacuum. The two values along the *x*-axis relate to the mass spectrometer scan number (upper number) and the elapsed time (lower number in min:s). The sample was heated from 50 (time 0:0) to 275 °C (3:45) at 60 deg/min then from 275 to 400 °C (time 10:00) at 20 deg/min. The probe temperature was held at 400 °C for the remaining scans.

Note also that ionization with 70-eV electrons produces doubly as well as singly charged molecular ions at m/z 360 and 420 for C_{60} and C_{70}, respectively. At 70-eV ionizing energy under our tuning conditions,[12] the major monoisotopic ions have m/z values of 360 (100), 420 (7), 672 (3), 696 (3), 720 (81) and 840 (3), where the numbers in parentheses represent the relative intensities of the ionic species. The ratio of C_{60}^{2+} to C_{60}^{+} is found to be 1.2, different from the value of 0.3 reported elsewhere.[5] The unusually abundant doubly charged molecular ions indicate the electronic stability of the C_{60} and C_{70} molecules. Appearance potential (AP) studies on C_{60} suggest that the second IP of C_{60} (and C_{70}) is less than 18 eV.[14] In addition, the ratio of C_{70} to C_{60} is different for the singly and doubly charged ions. At 400 °C probe temperature we obtain a ratio of about 0.05 for the singly charged ions and about 0.09 for the doubly charged ions by taking all the isotopic species into account and summing over 150 scans. This suggests that the electron impact ionization cross sections are different for C_{70} and C_{60}.

The above observations may help explain why Krätschmer et al., using sublimation to separate the C_{60} (and C_{70}) from the other carbon "soot", obtained a C_{70}-to-C_{60} ratio of only 0.02. We have observed C_{70}-to-C_{60} ratios as high as 0.28 using solvent extraction (see below).

2. Chemical Ionization. In order to further examine sample purity and to determine whether the weak signals seen at C_{58}^{+}, C_{56}^{+}, and at C_{68}^{+}, C_{66}^{+} in the 70-eV electron impact mass spectrum are due to fragmentation or are indigenous species, we used simultaneous positive and negative ion detection employing methane as a chemical ionization reagent gas. Proton transfer is the predominant ionization process producing positive ions, e.g. $C_{60}H^{+}$, whereas electron capture is the predominant process leading to negative ions, e.g. C_{60}^{-} formation.[15] In both processes, the ionic species produced contain only small amounts of internal energy, resulting in little or no fragmentation. Figure 2 shows the positive ion spectrum on the top and the negative ion spectrum at the bottom. The absence of the m/z 696 and 672 ions suggests that these two ions observed in the 70-eV spectrum are due to electron impact fragmentation and ejection of C_2 fragments rather than the presence of other C_{2n} species. As expected, for a "soft" chemical ionization process we see no evidence of doubly charged ions at m/z 360 and 420.

The intensity ratio between the molecular anion and protonated molecular ion is 15-to-1, indicating that electron capture is much more favorable than protonation for both C_{60} and C_{70}. Similar phenomena have been observed previously in the simultaneous positive and negative ion detection of highly condensed polynuclear aromatic hydrocarbons.[16] In fact, C_{60} and C_{70} can be considered as three-dimensional aromatic compounds in many of their physical and chemical properties.

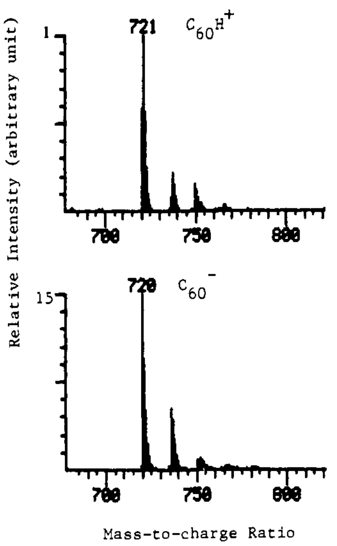

Figure 2. Positive ion (upper trace) and negative ion (lower trace) chemical ionization mass spectra of C_{60} with methane as a reagent gas.

B. High-Performance Liquid Chromatography (HPLC). A toluene extract obtained from the soot after ether wash was analyzed by normal phase HPLC. The separation was carried out on a Varian 5560 ternary gradient HPLC system equipped with a Hewlett-Packard HP-8450 Diode Array Detector (DAD) in series with an Applied Chromatography Model 750/14 evaporative mass detector (EMD). Good separation of C_{60} and C_{70} was achieved on a dinitroanilinopropyl (DNAP) silica (5-μm particle size, 300 Å pore diameter) with a gradient from *n*-hexane to 50% methylene chloride (Figure 3). The DAD (Figure 3a) monitors the separation at characteristic wavelengths for C_{60} and C_{70} at 330 and 384 nm, respectively, and shows the retention for C_{60} (peak near channel 230) and C_{70} (peak near channel 370). From the EMD measurements (Figure 3b) we obtain a C_{70}-to-C_{60} ratio of 0.28 for this sample. A semipreparative run (without the EMD) yielded purified C_{60} and C_{70} fractions whose UV-vis spectra appear to be identical with those reported by the UCLA group.[5]

The chromatographic characteristics of C_{60} and C_{70} closely resemble planar molecules with the corresponding "molecular footprints". As indicated in Figure 3, the retention of C_{60} on the charge-transfer DNAP surface is very similar to that of triphenylene, a C-18 planar molecule, while the C_{70} retention lies somewhere between models of the 5-ring (benzo[*a*]pyrene) and the 6-ring (coronene) compounds. Nondek et al.[17] have suggested that the retention of planar polynuclear aromatic hydrocarbons on DNAP can best be described in terms of the electronic character of the molecules, i.e. the difference between the highest occupied molecular orbital (HOMO) of the compound and that of naphthalene. He also reported a reasonably good correlation between the retention and the molecular area for this series of molecules. A 60-atom planar carbon cluster is estimated to be thermodynamically less stable than spheroidal C_{60}.[18] Thus the early elution for C_{60} may be considered as an extreme example of the effect of nonplanarity on retention time which has been well documented with smaller molecules in reverse-phase HPLC.[19]

C. Infrared Spectroscopy. Samples of C_{60} and C_{70} purified by preparative HPLC (vide supra) were dissolved in toluene and aliquots of these solutions were deposited onto KBr plates. Evaporation of the solvent left thin polycrystalline deposits of the

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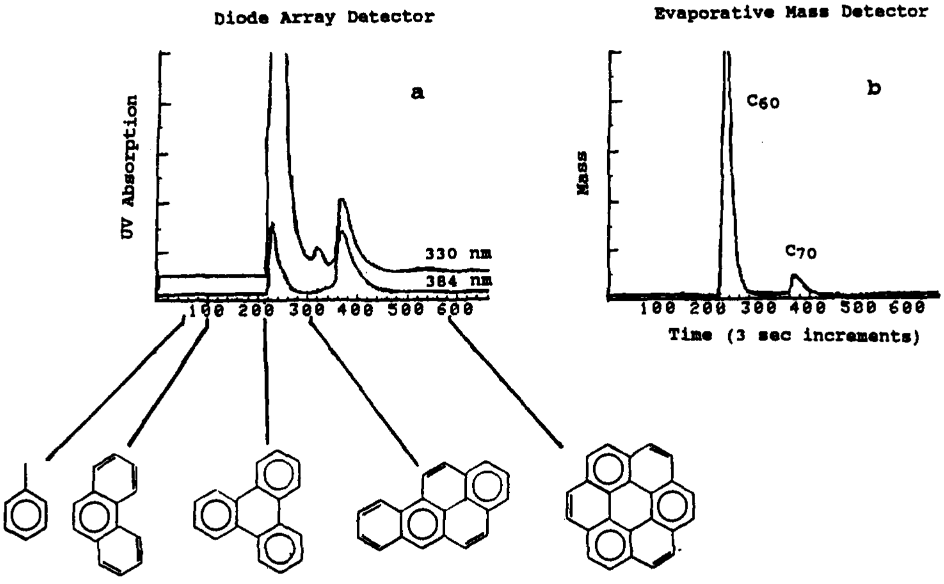

Figure 3. HPLC chromatograms of C_{60} and C_{70} on dinitroanilinopropyl silica with linear gradient at 1.5 mL/min from 100% n-C_6 at 50% CH_2Cl_2 over 35 min: (a) diode array detector response at 330 nm (upper trace) and 384 nm (lower trace); (b) evaporative mass detector. The ratio of C_{70} to C_{60} is given by the ratio of the areas of the two peaks in (b) and is 0.28 for this sample. Note, the x-axis time is expressed in 3-s increments. For comparison, retention times for different planar molecules (toluene, phenanthrene, triphenylene, benzo[*a*]pyrene and coronene) on this column are also illustrated.

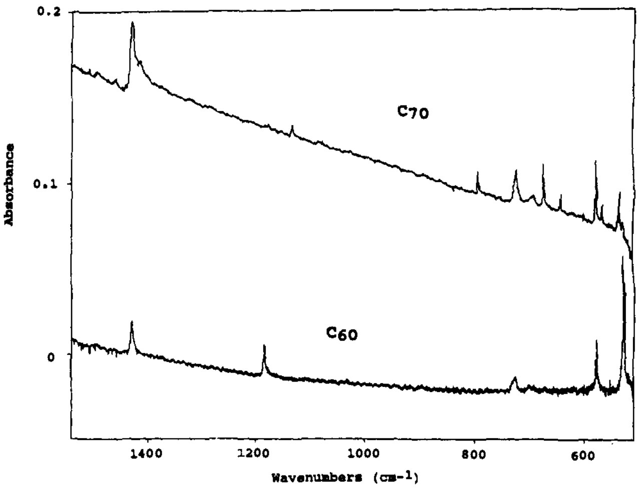

Figure 4. FTIR spectra of C_{60} (a) and C_{70} (b) on KBr substrates recorded at 0.5-cm^{-1} resolution from 1500 to 500 cm^{-1}. No absorptions are observed from 1500 to 4000 cm^{-1}.

solids suitable for infrared analysis. FTIR spectra were measured at 0.5-cm^{-1} resolution on a Mattson Sirius 100 spectrometer with a wide-band MCT detector and are ratioed to spectra of the clean KBr windows. Between 400 and 500 cm^{-1}, spectra were recorded on a Perkin-Elmer 684 dispersive instrument. The IR spectrum of purified C_{60} (Figure 4a) is dominated by sharp (<7-cm^{-1} half-width) absorptions at 1429, 1181, 576, and 527 cm^{-1}. These have been previously assigned to the four dipole-active vibrational modes of a C_{60} skeleton with icosahedral symmetry.[1,2,20-22] A weak and broad band at 725 cm^{-1} remains unassigned at this point as it also appears in IR spectra of other C_x chromatographic fractions. Notably absent are the multiple additional weak bands seen in spectra of sublimed C_x films.[2] We believe those additional features are largely due to C_{70}.

At least 14 discernable IR bands are seen in the spectrum of purified C_{70} (Figure 4b). Their peak positions match those of impurity bands reported for sublimed or solvent-deposited C_x films (Table I). Mode-specific assignment of these bands is not possible in the absence of further theoretical work. Nonetheless, establishing the C_{70} IR "fingerprint" is desirable for at least qualitative compositional analysis of crude C_x mixtures. This task is complicated by the coincidence (or near coincidence) of several major C_{60}/C_{70} absorptions (Table I). Of the four C_{60} IR bands, three at 1429, 576, and 527 cm^{-1} lie very close to C_{70} absorptions. The relative intensities of these three bands are very different for the two species which in part explains the widely varying relative intensities of the band envelopes seen in C_x mixtures.[1,2] However, isolated IR features unique to C_{60} or C_{70} are identifiable. C_{60} has a sharp band at 1181 cm^{-1}, where C_{70} does not absorb. Similarly, the presence of C_{70} is indicated by the appearance of bands at 1132, 795, 674, 642, and 458 cm^{-1}. We are presently employing a similar analysis to identify the unique vibrational features of even larger C_x species.

Table I. Infrared Band Positions and Relative Integrated Intensities for C_{60} and C_{70} Purified by Preparative HPLC (Spectra Were Measured down to 400 cm^{-1})

C_{70}		C_{60}		C_{60}/C_{70} mixture[a]	
freq, cm^{-1}	rel area	freq, cm^{-1}	rel area	freq cm^{-1}	rel area
1430.1 1427.9 1419.7 1413.0	1.00	1428.9	0.30	1429	1.00
1132.6	0.03	1181.2	0.28	1183	0.20
795.2	0.04			796	0.04
723.6	0.16	724.0[b]	0.20		
692.7	0.04				
674.2	0.07			675	0.06
642.2	0.02			643	0.03
577.8	0.11	576.3	0.28	577	0.20
565.6	0.02			565	0.03
535.1	0.08			536	0.04
458.0		527.3	1.00	528	0.70

[a] Data for evaporated carbon dust taken from ref 1. [b] Sample-to-sample variations in the relative intensity of this band suggest it is not due to C_{60}.

D. Electron Spin Resonance. The ESR spectrum of the C_{60} sample, recovered by a toluene rinse of the KBr pellet, showed no evidence for any carbon radical or dangling bonds, i.e. no free electrons within the 10^{13} spins/g sensitivity of the Bruker ESR 300 system used for these measurements. An ESR study of the sample prior to the ether extraction, however, showed evidence for non-spin-paired electrons. Thus, C_{60} exhibits no detectable

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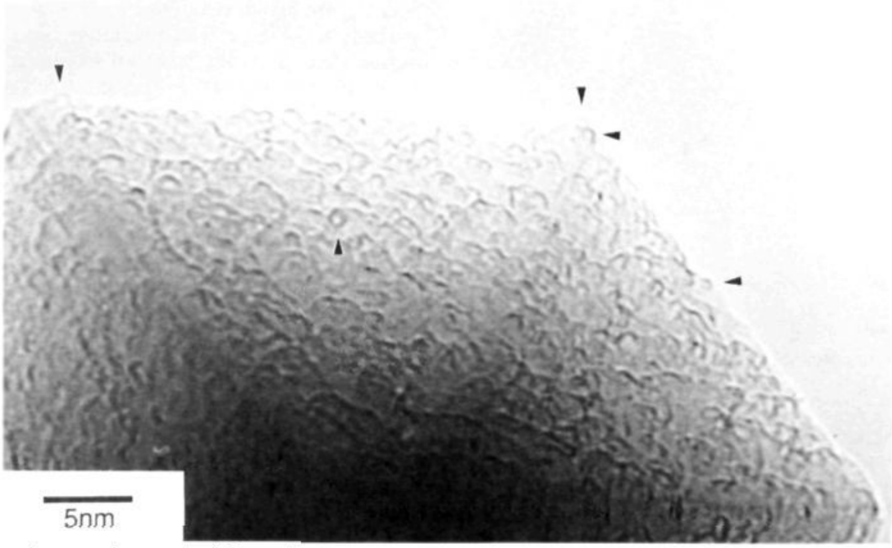

Figure 5. Transmission electron micrograph of C_{60} molecules on the surface of a single crystal of MgO.

ESR signal at room temperature.

E. Nuclear Magnetic Resonance. NMR studies of the non-ether treated material redissolved in CCl_4 or toluene show the strongest signal at 143 ppm assigned to the C_{60}, in agreement with other NMR studies reported by groups at Sussex,[3] IBM,[4] and UCLA.[5] In order to detect evidence of C_{70} much longer averaging was necessary since the C_{70} concentration in this particular sample was significantly lower. Five weak lines at 150.4, 147.9, 147.2, 145.2, and 130.9 ppm are in reasonable agreement with the 10, 20, 10, 20, 10 intensity ratio expected for C_{70}, again in agreement with similar results from other laboratories.[3,5] From the relative intensities we find that C_{70}-to-C_{60} ratio is about 0.19 in this particular sample.

F. Transmission Electron Microscopy of C_{60} on MgO. With use of transmission electron microscopy, images which we believe to be individual C_{60} (or C_{70}) molecules have been obtained. Since the phase contrast from typical amorphous supports such as silica or carbon often confuses the search for particles with diameters below 1 nm, we chose to evaporate a droplet of C_{60} in toluene onto a holey carbon film containing 20–100-nm microcrystals of magnesium oxide. Platelets of MgO have been used to visualize single atoms of gold because of the low contrast of this support.[23] Edges of some of the MgO crystals hang over holes in the support film and make it possible to observe clusters with little or no support material.

Figure 5 is an electron micrograph of a MgO crystal upon which C_{60} has been deposited. Circular contrast patterns with about a 0.8-nm diameter are observed,[24,25] a size consistent with that expected for individual C_{60} or C_{70} clusters. Note that circular images of about 0.8 nm also are observed further in from the edge. Although we feel it is improbable, such a pattern could be due to two or more spheroidal clusters aligned parallel to the electron beam axis. The particles appeared to be stable in position as several images were obtained from the same region.

We are presently modeling the image contrast of a through-focus series for spheroidal C_{60} molecules. Image simulation should make it possible to determine whether or not single C_{60} clusters, or more than one viewed end on in a line, are responsible for the observed circular features. Since the size range of the objects observed is consistent with that observed by STM, with theory,[26] and with that previously suggested in observations by Iijima,[27] we conclude that the use of MgO supports facilitates observation of individual C_{60} or C_{70} clusters.

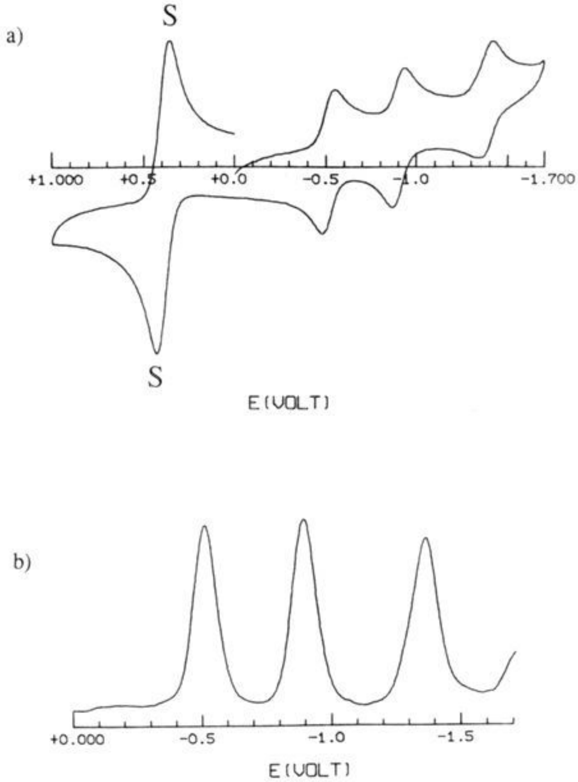

Figure 6. (a) Cyclic voltammogram of purified C_{60} in toluene/dichloromethane, glassy carbon electrode, 0.1 M tetrabutylammonium hexafluorophosphate, 100 mV/s scan rate vs SCE; (b) differential pulse polarogram. The internal standard, ferrocene/ferrocenium, is marked "S".

G. Electrochemistry. Purified C_{60} and C_{70} samples have been examined by cyclic voltammetry (CV) and differential pulse polarography (DPP).[28] Three reversible one-electron reduction waves and several irreversible ones are observed between +1.0

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(24) The nominal point-to-point resolution for the Philips EM420ST transmission electron microscope used in these experiments and operated at 100 kV was 0.3 nm.

(25) Crystals upon which only toluene was evaporated showed no evidence for C_{60}, *i.e. circular contrast patterns.*

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(28) After this work was completed the preprint by R. E. Huffler et al.[9] describing only two reversible CV waves for mixtures of C_n clusters was made available to us. In this study a different supporting electrolyte and solvent system is used.

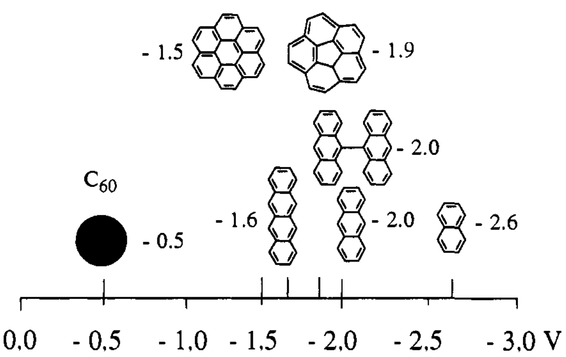

Figure 7. First reduction potential vs number of aromatic rings for selected hydrocarbons.

and –1.7 V by CV (Figure 6a) and DPP (Figure 6b). The values of the DPP peak potentials (vs. SCE) for the purified samples are –512, –900, and –1382 mV for C_{60} and –516, –888, and –1304 mV for C_{70}. Under our experimental conditions the ferrocene/ferrocenium redox potential is +394 mV. Irreversible reductions are observed for C_{60} at –1514 mV and at lower potentials. Unlike C_{60}, a major reduction process starts at about –1600 mV for C_{70}. No oxidation waves are observed up to +1000 mV for either molecule.

These results demonstrate the reversible formation of relatively stable C_n^-, C_n^{2-}, and C_n^{3-} (n = 60, 70) anions in solution.[29] While the differences between the first and second half-wave potentials of C_{60} and C_{70} are within experimental uncertainty, the 78-mV difference between their third reduction potentials appears to be significant. The differences between the redox potentials of C_{60} relative to C_{70} indicate that it is easier to add electrons to the C_{70} dianion compared to its C_{60} counterpart. This observation is consistent with a simple charge separation delocalization model. Since C_{70} presumably is larger than C_{60}, adding electrons to the anions would be easier if the negative charges are separated by larger distances or if they can be delocalized over a large number of carbon atoms. Interestingly, the first redox potentials of C_{60} and C_{70} are higher than those known for other aromatic hydrocarbons (see Figure 7) in qualitative agreement with the observation that the redox potential increases with the number of aromatic carbon rings.

The observation that three electrons can be added reversibly to C_n clusters is somewhat at odds with the theoretical prediction that C_{60} will add at most one electron.[30] Theoretical calculations however clearly indicate a triply degenerate LUMO,[3,18,31] which suggests to us that at least 3 electrons should be added relatively easily. A more quantitative description of the orbitals in doubly and triply charged anions should be helpful. It is worth mentioning in this context that C_n species containing up to *three* potassium atoms[32] as well as *one* trivalent lanthanide[33] per C_{60} cluster have been observed in the gas phase by mass spectrometry suggesting that C_n^{x-} ($x \leq 3$) anions exist in the gas phase. The distribution of electrons in the anionic clusters remains to be determined.[34]

Conclusions

The discovery by Krätschmer et al.[1,2] of a technique to produce and separate macroscopic quantities of the all carbon C_{60} molecule was a required first step in opening the door for exploring the molecular and bulk properties of this novel species. It is likely that C_{60} and C_{70} (as well as other C_n) pure carbon molecules and their associated derivatives shortly will be available in substantial quantity, opening the way to exploiting these materials in such diverse areas as organic chemistry, lubrication, materials science, solid-state physics, energy storage, polymer science, and catalysis.

Acknowledgment. We acknowledge the technical assistance of G. J. Dechert in obtaining mass spectral data. We thank the following people for providing preprints prior to publication, Prof. Richard Smalley, Prof. Robert Whetten, and Dr. Donald Bethune.

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(29) Similar results are obtained when tetrahydrofuran, sodium tetraphenyl borate, or platinum button electrodes are used.

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(34) Magnetic resonance techniques are currently employed to examine the *reduced* carbon clusters.

Synthesis of [(mes)OsH(CH_3)CO] from [(mes)OsCl_2]$_n$ and C_2H_5OH. Controlled Fragmentation of Ethanol into CH_3, H, CO, and H_2 by a Transition-Metal Center

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Abstract: In contrast to the reaction of [(mes)OsCl_2]$_n$ (**1**; mes = mesitylene, 1,3,5-trimethylbenzene) with Na_2CO_3/EtOH under an ethylene atmosphere which gives [(mes)Os(C_2H_4)$_2$] (**3**), the corresponding reaction in the presence of propene leads to the formation of [(mes)OsH(CH_3)CO] (**2**) and [(mes)Os(η^3-C_3H_5)Cl] (**4**) in about equal quantities. If $H_2C{=}CH$-*t*-Bu is used instead of propene, only **2** is obtained. In the absence of olefin, the reaction of **1** with Na_2CO_3/EtOH gives [$(mes)_2Os_2(\mu\text{-OEt})_3$]Cl (**5**). Experiments done in C_2D_5OD (leading to **2**-d_4) and with propene in propan-2-ol (leading only to **4**) provide evidence that *all three ligands H, CH_3, and CO* coordinated to the metal center in **2** are generated from C_2H_5OH. This is the first example illustrating that a controlled fragmentation of a primary alcohol into an alkyl group, CO, H, and H_2 can occur, the added olefin being the trap of H_2.

Introduction

Hydrido–transition-metal complexes are usually prepared from halogeno metal derivatives and compounds such as $NaBH_4$, $LiAlH_4$, or Na[$AlH_2(OC_2H_4OMe)_2$] (red-al) as the hydride source.[1] There are, however, also reports in the literature[2,3] that hydrido as well as carbonyl hydrido complexes can be obtained more simply on treatment of chloro, bromo, or iodo metal com-

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