8634 J. Phys. Chem. 1990, 94, 8634-8636

Efficient Production of C_{60} (Buckminsterfullerene), $C_{60}H_{36}$, and the Solvated Buckide Ion[†]

R. E. Haufler,[‡] J. Conceicao,[‡] L. P. F. Chibante,[‡] Y. Chai,[‡] N. E. Byrne,[‡] S. Flanagan,[‡] M. M. Haley,[‡] S. C. O'Brien,[§] C. Pan,[‡] Z. Xiao,[‡] W. E. Billups, M. A. Ciufolini, R. H. Hauge, J. L. Margrave, L. J. Wilson, R. F. Curl, and R. E. Smalley*

Rice Quantum Institute, Rice Institute for Biochemical and Genetic Engineering, and Departments of Chemistry and Physics, Rice University, Houston, Texas 77251 *(Received: October 4, 1990)*

Buckminsterfullerene, C_{60}, was prepared in gram quantities by contact-arc vaporization of a graphite rod in a 100-Torr atmosphere of helium, followed by extraction of the resultant graphitic soot with toluene. The dominance of C_{60} in this extract was verified by mass, FTIR, and NMR spectroscopy. The molecule was successfully hydrogenated to $C_{60}H_{36}$ via a Birch reduction and dehydrogenated back to bare C_{60} by treatment with DDQ reagent. Cyclic voltammetry of C_{60} in methylene chloride revealed highly reversible formation of at least two stable anionic forms of C_{60} in solution. A broad new class of these fulleride and fulleronium ions is anticipated, both with the internal cavity empty and with any one of a large number of elements inside, thus providing a means of fine-tuning the chemical, optical, and redox properties.

Introduction

Recently Krätschmer, Huffman, and co-workers reported the first macroscopic preparation of C_{60} (buckminsterfullerene).[1,2] Bethune and Meijer have verified this work[3,4] and together with Tang and Rosen reported the vibrational Raman spectrum of a C_{60} film.[5] Kroto and co-workers[6] have used the Krätschmer–Huffman technique to prepare C_{60} and have reported ^{13}C NMR spectra of chromatographically separated C_{60} and C_{70} which confirm the spheroidal structures predicted[7,8] for these molecules (I_h and D_{5h} symmetry, respectively). Johnson et al.[9] have also reported the NMR spectrum of C_{60}. In the following short Letter we present a detailed description of an implementation of this Krätschmer–Huffman technique capable of producing gram quantities of C_{60} per day. Our intent is to provide a cookbook-level recipe for the production of C_{60} in sufficient quantities for general chemical experimentation. The method is sufficiently simple that most laboratories should be able to set up rapidly to generate their own samples of this important new material.

We also provide two initial examples of the sort of interesting new chemistry that is now available for study: (1) the first successful chemical reaction on the surface of C_{60} (hydrogenation to $C_{60}H_{36}$ and subsequent dehydrogenation back to C_{60}) and (2) the first generation of ionic forms of C_{60} in solution (by cyclic voltammetry). In view of the broad range of fullerenes which can potentially be produced by this Krätschmer–Huffman method, and the possibility that the method can also produce derivative versions of each of these with any of a wide range of elements trapped inside the central cavity, it seems likely that vast new areas of chemistry and materials science will soon be open for exploration.

The C_{60} Generator

Figure 1 presents a schematic diagram of the C_{60} generator used in this study. Here a 6 mm o.d. graphite rod is kept in contact with a graphite disk by gentle spring pressure. The surrounding walls were water-cooled copper shrouds forming a collection cylinder 8 cm i.d., 15 cm long. This apparatus was contained in a standard 6-in. UHV six-way conflat cross initially pumped to below 10^{-6} Torr with a 50 L s^{-1} turbo pump, but held near 100-Torr pressure of helium by slow pumping with a small mechanical rotary pump while bleeding in the helium at a rate of 1 sccm. Connection of the graphite rod and disk to an external ac (60 Hz) high-current power source was made with the copper clamps shown in the figure and two water-cooled vacuum feedthroughs. Vaporization of the graphite was then accomplished by driving a 100–200-A current between the two electrodes at an rms voltage of 10–20 V. The spring tension was adjusted to maintain the arc between these two nearly contacting electrodes such that the bulk of the power was dissipated in the arc and not in Ohmic heating of the rod. We call this a "contact arc" since it was clear that the best operation occurred when the electrodes were just barely touching. Generally, the process of starting up the apparatus was faciliated by sharpening (in a pencil sharpener!) the 6 mm o.d. graphite rod to a conical point.

To our knowledge the first use of such an arrangement was published by Krätschmer, Sorg, and Huffman in their study of matrix-isolated carbon clusters.[10] With the design parameters listed above, the 6-mm graphite rod was vaporized at the rate of 10 g/h. In practice, a volcano-shaped deposit quickly grew around the point of contact and had to be removed periodically. We suspect a better arrangement would have been to use two 6-mm rods driven against each other under computer control (with current and voltage feedback) in a completely symmetrical design.

After a few hours operation of this device, roughly 10 g of a black graphitic soot had been collected on the surrounding water-cooled copper surfaces. This material was then scraped together and placed in the thimble of a Soxhlet extractor. After 3-h extraction with boiling toluene a dark red-brown liquid was recovered which upon removal of the solvent in a rotary evaporator yielded a black powder, typically amounting to 10 ± 2% of the original graphitic soot.

Characterization of the Graphitic Soot Extract

The black powder toluene extract was found to behave much like that reported by Krätschmer et al.[2] Mass spectroscopy of ions generated by electron bombardment of vapors given off from the material on a standard heated probe readily showed the sample to be composed primarily of C_{60} and C_{70} with both the 1+ and 2+ ions clearly detected with the expected ^{13}C isotopic substructure. Knudsen effusion mass spectral measurements[11] yielded

---

[†] This paper is dedicated to our colleague, E. S. Lewis, who upon first hearing of the C_{60} soccerball conjecture in September of 1985 said, "Why don't you get some soot and extract it?"

[‡] Robert A. Welch Predoctoral Fellow.

[§] Present address: Texas Instruments, Dallas, TX.

(1) Kratschmer, W.; Fostiropoulous, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167.

(2) Kratschmer, W.; Lamb, L. D.; Fostiropoulous, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(3) Meijer, G.; Bethune, D. S. *J. Chem. Phys.*, in press.

(4) Meijer, G.; Bethune, D. S. *Chem. Phys. Lett.*, in press.

(5) Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J. *Chem. Phys. Lett.*, in press.

(6) Taylor, R.; Hare, J. P.; Abdul-Sade, A. K.; Kroto, H. W. *Chem. Commun.*, in press.

(7) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(8) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779.

(9) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.*, in press.

(10) Kratschmer, W.; Sorg, N.; Huffman, D. R. *Surf. Sci.* **1985**, *156*, 814.

0022-3654/90/2094-8634$02.50/0

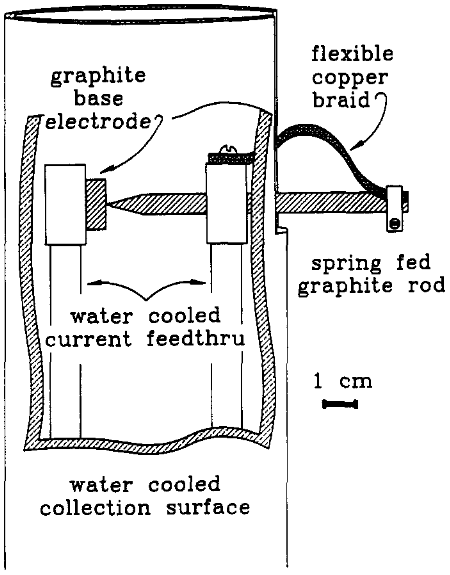

Figure 1. Schematic diagram of graphite rod contact-arc C_{60} generator.

an estimate of 21.5 kcal mol^{-1} for the heat of sublimation of C_{60}. The ^{13}C NMR of this mixture dissolved in C_6D_6 clearly displayed a single peak at 143.2 ppm, in excellent agreement with the spectrum reported by other groups.[6,9] The C_{70} content of this sample was too low to clearly reveal the five ^{13}C NMR peaks reported for this molecule by Kroto and co-workers.[6] On the basis of their reported spectra, we estimate the C_{70} content of the C_6D_6 solution to have been less than 15%. Fourier transform infrared spectroscopy (FTIR) of the C_{60} material pressed in a KBr pellet showed a pattern dominated by four strong peaks measured at positions (widths) of 1428.5 (6), 1182.4 (4), 576.4 (4), and 527.4 (3) cm^{-1}. A number of other weaker features probably due principally to C_{70} were evident as well, much like that reported by Krätschmer et al. for a sublimed thin film.[2]

In order to obtain an estimate of the magnitude of pertubation caused by the C_{60} crystalline matrix in these FTIR spectra, a matrix-isolation experiment was carried out using argon codeposited onto a gold substrate[12] cooled to 10 K along with C_{60} vapor sublimed from the raw graphitic soot extract. The resultant FTIR spectrum was considerably sharper than that of the C_{60} solid, but only slightly shifted in peak positions: 1431.9 (4), 1184.8 (2), 579.3 (2), and 530.1 (1) cm^{-1}. Essentially the same FTIR spectrum was observed from a krypton matrix, with no apparent shift in peak positions from that found with argon. These frequencies are therefore likely to be close to the gas-phase values.

Hydrogenation of C_{60} and Dehydrogenation of $C_{60}H_{36}$

C_{60} was found to undergo Birch reduction[13] (Li, liquid NH_3, *t*-BuOH), underscoring the aromatic character of the molecule. The dark-colored C_{60} was thus converted to a light cream to off-white substance, single spot by TLC (30% CH_2Cl_2 in hexanes, $R_f = 0.37$, UV inactive, revealed with I_2). The new substance began to darken at 170 °C, became brown at 260–270 °C, but did not melt by 305 °C. An ignition test showed that the material burns without leaving a residue. Spectral analysis of the reduced material produced the following results. MS (EI, 110 eV) indicated that two components were present. The more volatile component began to vaporize at a probe temperature of 260 °C at 3×10^{-7} Torr and showed signals at *m/e* 756 (M^+) and 378 (M^{2+}), indicative of a molecular formula $C_{60}H_{36}$. The less volatile component appeared at a probe temperature of ca. 360 °C, and it produced signals at *m/e* 738 (M^+) and 369 (M^{2+}), consistent with a formula $C_{60}H_{18}$. It is not clear at this point whether $C_{60}H_{18}$ is a genuine coproduct of the Birch reduction or whether it is a pyrolysis product of $C_{60}H_{36}$. No signals at *m/e* higher than 756 were observed at probe temperatures below 400 °C. This suggests that whatever product arose from Birch reduction of C_{70}, also present as a contaminant in the C_{60} sample, must have been insufficiently volatile under the conditions of our MS experiment to be detected. Above 400 °C, a small peak at *m/e* = 840 appeared, corresponding to C_{70}^+.

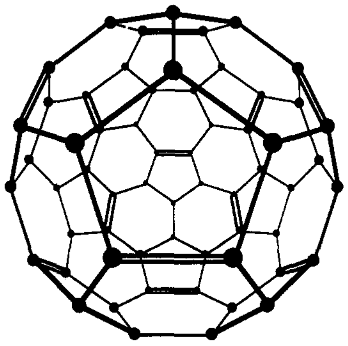

Figure 2. One possible isomer of $C_{60}H_{36}$ (the hydrogens are not shown) where the remaining 12 double bonds are isolated from each other, one on each pentagon. The view is from the perspective of an observer very close to the front surface of the molecule.

The proton NMR spectrum of reduced C_{60} (in $CDCl_3$) exhibited a broad multiplet between 4.2 and 2.5 ppm, with maxima at 3.80 and 3.35 ppm. This region of the spectrum was completely free from absorptions in the proton NMR trace of C_{60}. Interestingly, the chemical shift of the protons in dodecahedrane is 3.38 ppm.[14] The unusually broad shape of the absorption of reduced C_{60} is probably caused by the presence of isomers of $C_{60}H_{36}$ and possibly by the presence of $C_{60}H_{18}$.

We note that there is a simple explanation of this observation in that 36 is the number of hydrogens required to leave a single unconjugated double bond on each pentagon of soccer ball C_{60} and that there are many ways of arranging these double bonds while preserving the lack of conjugation (the Birch reduction should only attack conjugated double bonds).[13] Figure 2 shows one such isomer.

The IR spectrum (KBr) exhibited bands at 2925 (s), 2855 (s), 1620 (w), 1450 (w), 1400 (m), and 675 (s, sh) cm^{-1}, strongly suggesting the presence of C—H and C=C bonds in the new reduced material. The UV spectrum (cyclohexane) showed a single band peaked at 222 nm. The original C_{60} material, on the other hand, showed a number of strong absorptions in cyclohexane solution, the most prominent at 218, 258, 330, and 378 nm. This C_{60} absorption spectrum in solution is similar to that originally published for the solid C_{60} film by Krätschmer et al.[1,2]

Treatment of a toluene solution of the Birch-reduced product with DDQ[15] (reflux) caused rapid discharge of the red color of the DDQ–toluene complex and formation of a dark brown solution, similar in appearance to solutions of C_{60}. TLC analysis showed that the Birch product had been completely converted into a new substance that was indistinguishable from authentic C_{60}. Mass spectral analysis confirmed that the product obtained from this reaction was virtually exclusively C_{60} (*m/e* 720), contaminated with a minor amount of C_{70}. *Thus, the reduction of C_{60} appears to be fully reversible*, suggesting that no alteration of the molecular skeleton occurred upon Birch reduction.

Cyclic Voltammetry of C_{60}

The electrochemical properties of C_{60} were probed by cyclic voltammetry of the material dissolved in CH_2Cl_2 and kept under a nitrogen atmosphere. The solution also contained $[(n\text{-}Bu)_4N]BF_4$ (0.05 M) as a supporting electrolyte and ferrocene, Fc (0.05 M), for use as an internal standard. Figure 3 displays a typical cyclic

---

[11] Margrave, J. L.; Paule, R. C. Free Evaporation and Effusion Techniques. In *Characterization of High Temperature Vapors*; Margrave, J. L., Ed.; Wiley-Interscience: New York, 1967; pp 130–151.

[12] Hauge, R. H.; Fredin, L.; Kafafi, Z. H.; Margrave, J. L. *Appl. Spectrosc.* **1986**, *40*, 588.

[13] Review: Kaiser, E. M. *Synthesis* **1972**, 391.

[14] Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *J. Am. Chem. Soc.* **1983**, *105*, 5446.

[15] Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317.

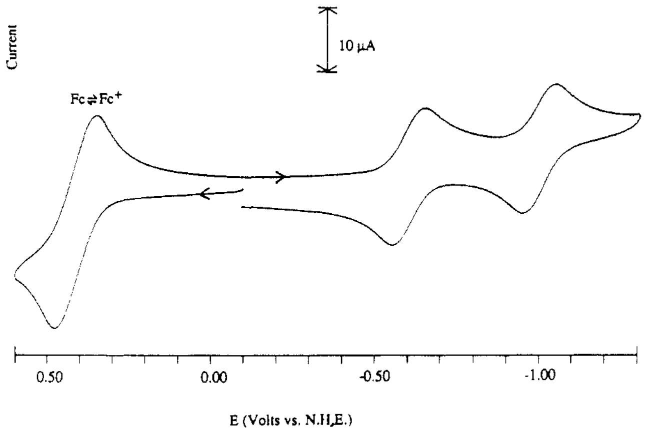

Figure 3. Cyclic voltammetry of C_{60} in CH_2Cl_2 (0.05 M $[(n\text{-Bu})_4N]BF_4$) at a glassy carbon button electrode. Sweep rate: 100 mV s^{-1}. Internal standard: ferrocene/ferrocenium couple at +0.40 V vs NHE.

voltammogram of this solution obtained by using a glassy carbon working electrode, referenced to the normal hydrogen electrode (NHE). A platinum wire was used as an auxiliary electrode in the three-electrode geometry of this standard BAS CV27 apparatus. As is evident in Figure 3, C_{60} undergoes facile electrochemical reduction under these conditions in two waves. Measured from the Fc/Fc+ internal standard[16] the $E_{1/2}$ values for the two successive reduction waves of C_{60} are at -0.61 and -1.00 V relative to NHE. Similar results were obtained with a platinum button working electrode.

With ΔE_p's of 100 and 110 mV, respectively, these reduction processes are clearly quite reversible. In fact, they appear to be more reversible than that of the Fc/Fc+ couple (ΔE_p = 130 mV) used here as an internal standard. This is to be expected for the rigid, highly symmetrical structure now proven to be correct for this molecule. Both of the C_{60} reduction reactions were determined by coulometry to be one-electron processes and presumably correspond to

$$C_{60} \overset{e^-}{\rightleftharpoons} C_{60}^- \overset{e^-}{\rightleftharpoons} C_{60}^{2-}$$

electrochemical reactions. Further, less reversible reductions were also observed to occur in this CH_2Cl_2 solution at more negative potentials than explored in the cyclic voltammogram of Figure 3. As argued by Haddon, Brus, and Raghavachari,[17] the t_{1u} lowest unoccupied orbital of C_{60} can hold up to six extra electrons, and highly charged negative ions of C_{60} may be expected to be stable in some solutions. This is also reasonable in view of the relatively high electron affinity of 2.8 eV measured previously for C_{60} by photoelectron spectroscopy.[18] The two highly reversible reduction waves seen in Figure 3 for C_{60} in CH_2Cl_2 suggest that it should be possible to electrochemically produce stable "buckide" salts. These may have many applications as new materials, perhaps even extending to a new class of rechargeable batteries, and may provide single crystals for X-ray diffraction studies.

No electrochemical oxidations were observed out to +1.50 V (NHE) with the C_{60} dissolved in CH_2Cl_2 or nitrobenzene. The ionization potential of C_{60} has recently been measured by Zimmerman et al.[19] by charge-exchange bracketing techniques in a series of impressive FT-ICR experiments. Their result of 7.50–7.72 eV is quite high, both in comparison to the other fullerenes in this size range and for carbon clusters in general. (Note that the work function of carbon is 4.9 eV.[20]) A high oxidation potential for C_{60} in these type of solutions therefore seems reasonable.

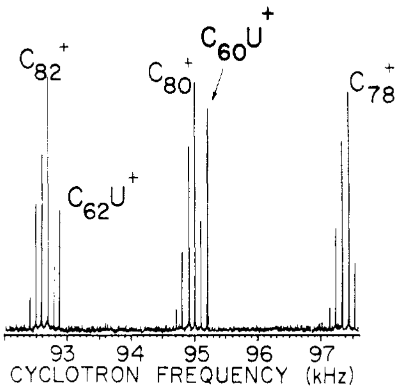

Figure 4. FT-ICR of $[C_{60}U]^+$ and other fulleronium ions generated by laser vaporization of a graphite disk impregnated with UCl_3.

One of the most intriguing challenges for future research in this new area will be the study of metallofullerenes such as $C_{60}K$ where the metal atom is trapped inside the fullerene cage. Such metal-containing molecules are likely to be much more readily oxidized in solution. Previous supersonic cluster beam experiments[9,18,21] have provided strong evidence for the generation of such species where the metal is La, Ca, Ba, Sr, Na, K, and Cs. As an extreme example, consider Figure 4 which shows FT-ICR mass spectral evidence for the formation of $C_{60}U$ as a positive ion, produced by laser vaporization of a graphite disk impregnated with UCl_3. It therefore seems likely that any actinide or lanthanide may be successfully incorporated into C_{60}. Since the inner cavity of C_{60} is large enough to hold at least the positive ion of any element, the range of possible materials of this type may be very large. A critical future avenue for research will be the adaption of the Krätschmer–Huffman technique to the incorporation of metal atoms.

Conclusion

These substances may require a new and divergent meaning for the terms "outer sphere" and "inner sphere" in describing organometallic complexes. For the fullerenes there is no doubt that there will be a rich chemistry associated with the "outside" of the molecule. We have given one such example here in the formation of $C_{60}H_{36}$. True outside complexes will certainly also exist for these fullerenes with a wide range of metals and ligands. But the fullerenes possess a unique sort of "inside" space as well. Here a wide range of atoms from throughout the periodic table may reside, perhaps with little direct influence on the overall "outside" chemistry. Although chemically rather hidden, their ability to fine-tune the optical and redox properties of the fullerenes may be highly useful.

Acknowledgment. We thank D. S. Bethune, K. Fostiopolis, H. W. Kroto, W. Krätschmer, J. R. Heath, D. R. Hoffman, L. Lamb, and T. G. Schmaltz for stimulating conversations and for communication of their results prior to publication, A. M. Kook and T. D. Marriott for help with the NMR and mass spectroscopy, and F. D. Weiss and J. L. Elkind for assistance in obtaining the FT-ICR spectrum of $C_{60}U^+$. This research was supported in part by the National Science Foundation, the Robert A. Welch Foundation, the Office of Naval Research, the U.S. Army Research Office, the Department of Energy, Division of Chemical Sciences, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

---

(16) Gagne', R. R.; Koval, C. A.; Lisensky, G. D. *Inorg. Chem.* **1980**, *19*, 2854.

(17) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459.

(18) Curl, R. F.; Smalley, R. E. *Science* **1988**, *242*, 1017.

(19) Zimmerman, J. A.; Eyler, J. R.; Bach, S. B. H.; McElvany, S. W. *J. Chem. Phys.*, in press.

(20) Willis, R. F.; Feuerbacher, B.; Fitton, B. *Phys. Rev.* **1971**, *B4*, 2441.

(21) Weiss, F. D.; Elkind, J. L.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *J. Am. Chem. Soc.* **1988**, *110*, 4464.